# SYSTEM OF CHEMISTRY

OF

# INORGANIC BODIES.

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# PART II.

# OF PRIMARY COMPOUNDS.

By the term primary compound, is meant a combination of two or more simple bodies with each other. Thus potash is a primary compound, being composed of potassium and oxygen united together. Cyanogen is another of these compounds, being composed of carbon and azote united in definite proportions; as is also arsenic acid, which is a definite compound of arsenic and oxygen. Almost every one of these primary compounds have been noticed at least in the first part of this work, in which almost all the known direct combinations of the simple bodies with each other have been noticed. But it will be requisite in this second part to treat of the most important of them in greater detail than could be done with propriety while treating of the simple bodies. Now all the primary compounds naturally divide themselves into three classes, namely, acids, alkalies or bases, and neutrals. These three classes will be described in succession in the three following chapters.

#### CHAP. I.

#### OF ACIDS.

By acid at present is understood a substance, which has the property of combining with and neutralizing alkalies or bases. Formerly it was considered as requisite that bodies, in order to belong to the class of acids, should have a sour taste, should be soluble in water, and should have the property of reddening vegetable blue colours—and these properties do indeed belong to some of the most common and powerful acids; but there are various acids which have no taste, and which are not sensibly soluble in water, and some which are incapable of altering the colour of the most delicate vegetable blues. All the acids with which we are at present acquainted are compounds.

Part II.

Chap. I.

Lavoisier endeavoured to prove that oxygen constitutes an essential constituent in them all. And this opinion holds good with the greater number of acids which chemists were acquainted with in his time, though not with the whole of them.

Consist of nine classes,

It is now known that not merely oxygen, but all the other simple supporters, namely, chlorine, bromine, iodine, and fluorine, are capable of forming acids, by uniting with several of the acidifiable bases, and indeed also when they unite with several of the alkalifiable bases; especially those belonging to the last family, and described under the name of noble metals. In fact the greater number of the metals belonging to this family, are scarcely entitled to the name of alkalifiable bases; though they hardly possess sufficiently energetic characters to entitle their compounds, if we except their chlorides, to be considered as acids.

Besides the five supporters, cyanogen, sulphur, selenium, and tellurium, have also the property of forming acids when they unite with the acidifiable bases. Indeed it is not improbable that this property may belong to most if not to the whole of the acidifiable bases, though at present it has only been ascertained to hold with respect to those which have been just named. Thus it appears that the acids at present known may be divided into 9 classes, namely,

Oxygen acids,
 Chlorine acids,

6. Cyanogen acids,7. Sulphur acids,

3. Bromine acids,

8. Selenium acids,

4. Iodine acids,

9. Tellurium acids.

5. Fluorine acids,

These 9 classes of acids will be described in succession, so far as the present imperfect state of the science will enable us to go.

#### CLASS I.

# OXYGEN ACIDS.

The acids which contain oxygen as an essential constituent, have been longer known and more carefully examined by chemists than those which constitute the other eight classes. This is probably the reason why they are at present so much more numerous than all the other acids put together. There can be no doubt that the chlorine acids, and those belonging

to each of the other classes, will increase very much in number as the science extends.

Div. I.

The oxygen acids are of two kinds. Some consist of oxygen united to a single acidifiable base or a single supporter. sulphuric acid is a compound of sulphur and oxygen; carbonic acid of carbon and oxygen; and bromic acid of bromine and But there are a considerable number of oxygen acids in which the oxygen is united at once with two and sometimes Thus acetic acid is a compound of oxygen, with three bases. carbon, and hydrogen; while uric acid is a compound of oxygen, carbon, hydrogen, and azote. This second set of acids is very numerous. They either exist ready formed in the vegetable and animal kingdoms, or they are formed from vegetable and animal bodies by certain chemical processes. therefore, subdivide the oxygen acids into

- 1. Acids with a single base.
- 2. Acids with a compound base.

The first of these divisions includes the most important of those acids that are employed as instruments of chemical investigation. But there are also several of the acids with compound bases that are nearly indispensable in a chemical laboratory, for some of the most frequent and useful processes which the practical chemist has occasion to perform. reasons make it indispensable for us to take a view of these acids in this part of the work.

### DIVISION I.-ACIDS WITH A SIMPLE BASE.

The oxygen acids with a simple base, so far as we are at Table of sim-Their ple oxygen present acquainted with them, amount to about 36. names are as follows:

1.	Perchloric,
2.	Chloric,
3.	Chlorous,
4.	Bromic,
<b>5.</b>	Iodic,
6.	Nitric,
7.	Nitrous,
8.	Hyponitrous

9. Carbonic.

10. Oxalic, 11. Boracic, 12. Silicic.

13. Phosphoric,

14. Pyrophosphoric,

15. Phosphorous,

16. Hypophosphorous,

17. Sulphuric,

18. Sulphurous,

19. Hyposulphurous,

20. Subsulphurous,

21. Hyposulphuric,

22. Selenic,

23. Selenious,

24. Telluric.

Chan	T
c nap,	ъ,

25. Arsenic,	31. Molybdic,
26. Arsenious,	32. Tungstic,
27. Antimenic,	33. Columbic,
28. Antimonious,	34. Titanic,
29. Chromic,	35. Manganesious,
30. Uranic,	36. Manganesic.

I shall take a view of each of these acids in succession.

## SECTION I .-- OF THE ACIDS OF CHLORINE.

Chlorine and oxygen unite in three different proportions so as to form acids. These are

		lorine.		kygen.
1.	Chlorous acid	1 atom	+	3 atoms
	Chloric acid	1	÷	
3.	Perchloric acid	1	+	7

blorous

These three acids have been described in Vol. I. p. 66; the first under the name of quadroxide of chlorine. It has been generally considered as an oxide, because when we attempt to unite it with a base, it undergoes decomposition. However, if it be placed in contact with an alkaline base in its nascent state, a combination takes place, and a chlorite is formed having a peculiar and acrid taste similar to that of the acid. These salts have the property of destroying vegetable colours. There can be little doubt that Von Stadion's analysis is accurate, so that it is a compound of

1 atom chlorine	•		4.5
3 atoms oxygen	•	•	3
			7.5

and its atomic weight is 7.5.

The facts respecting chloric and perchloric acids stated in the first volume of this work, constitute every thing hitherto ascertained respecting them.

The circumstance of two substances, both of which are so strongly negative, as oxygen and chlorine, uniting together, seems at first sight rather incompatible with the electric theory of chemical affinity. I have endeavoured to obviate this difficulty in the Introduction to this work (Vol. I. p. 39). The affinity between the oxygen and chlorine is obviously weak. Hence heat which seems to increase the intensity of the negative electricity of chlorine; easily occasions a decomposition of these acids.

# SECTION II. -OF THE ACIDS OF BROMINE AND IODINE.

The oxygen acids of bromine and iodine hitherto observed are only I acid for each of these bodies, constituting bromic and iodic acid, analogous as their mames imply to chloric acid. Their properties have been already described in p. 74 and p. 82 of the first volume of this work. I do not notice here the iodous acid of Sementini, nor the hypiodous acid of Mitcherlich, because I have already stated all the facts respecting these supposed acids with which I am acquainted. Bromic acid is a compound of

1 atom bromine		•	•	10
5 atoms oxygen	•	•	•	5
				*******
				15

and iodic acid of

1 atom iodine	•	•	15.75
5 atoms oxygen	•	•	5
			20.75

Iodous acid (if it exist) ought, from analogy, to be a compound of

l atom iodine	•	•	15.75
3 atoms oxygen	•	•	3
			18.75

#### SECTION III. -- OF THE ACIDS OF AZOTE.

Azote and oxygen combine in three proportions, forming the three acids which have been called *nitric*, *nitrous*, and *hyponitrous* acids.\*

\* When the French chemists contrived their new chemical nomenclature in 1787, a base was supposed to be capable of uniting only with two doses of oxygen, and of forming two acids. They distinguished these acids by making the acid containing most oxygen terminate in ic, and the one containing least in ous. Thus nitric acid contains most oxygen, and nitrous acid least. It was afterwards discovered that in some cases acids exist containing less oxygen than those in ous. These are distinguished by prefixing the syllables hypo, as hyponitrous. The mode is still imperfect. For some bases unite with four or even five doses of oxygen, and form four or even five acids.

Chap. I.

## 1. Nitric Acid.

listory.

This acid, which is one of the most important instruments of investigation of which the chemist is possessed, was certainly known to Geber, an Arabian chemist of the 7th century, and the author of the first purely chemical work with which we are acquainted. It is always procured from saltpetre or nitre, a salt which forms spontaneously or the surface of the earth in most parts of the world. The saltpetre, made use of in this country, is imported from India, where it is collected in great quantities from the soil. It is afterwards refined in Great Britain, and made fit for the manufacture of gunpowder, in which by far the greatest part of the saltpetre imported is expended. Saltpetre is a compound of nitric acid and potash. If sulphuric acid be mixed with it, the nitric acid is disengaged, and may be distilled over from a glass retort into a receiver. Nitric acid cannot be obtained free from water, but the sulphuric acid of commerce always contains a sufficient quantity of water to supply the nitric acid with that essential element.

How obtain.ed.

To prepare nitric acid, the best way is to put 12.75 parts of saltpetre into a retort, and to pour over them 12.25 parts of the sulphuric acid of commerce (of the specific gravity 1.847). Lute an adopter to the beak of the retort, and fit the extremity of the adopter into the mouth of a glass receiver amply large enough to hold all the nitric acid which will come over. The retort being placed in a sand bath and a fire kindled below it, the mixture of nitric and sulphuric acid speedily becomes liquid, and the whole nitric acid may be distilled over at a moderate temperature, and without any loss. The anhydrous nitric acid contained in 12.75 parts of nitre is 6.75, and the water contained in 12.25 of sulphuric acid is 2.25. But if the heat applied be not too great, one-half of this water remains in the retort united to the salt of potash formed by the sulphuric acid, so that the quantity of nitric acid obtained should weigh 7.875 parts, and its specific gravity should be 1.55. But in general a little more than one-half of the water comes over, so that the specific gravity of the nitric acid obtained is rarely so high as 1.5. the heat applied be a little too high, all the water in the sulphuric acid comes over with the nitric acid. The quantity of nitric ' acid obtained in that case is 9 parts, and its specific gravity is This is by far the most common strength of nitric acid obtained by this process.

If instead of 12.25 of sulphuric acid we mix only 6.125 parts

with 12.75 of nitre, only two-thirds of the nitre is decomposed and comes over into the receiver, combined with all the water in the sulphuric acid. When this portion has passed over, the saline matter in the retort becomes solid. If we increase the heat so as to liquefy this salt, it swells up in consequence of the decomposition of the remaining portion of nitric acid, which cannot be distilled over, because there is no more water with which it can combine. It is resolved into deutoxide of azote and oxygen gas. The deutoxide of azote is absorbed by the nitric acid already distilled over, to which it communicates a red colour, and the property of fuming strongly when exposed to the air. In this state it is distinguished by the name of fuming nitric acid. The oxygen gas makes its escape, or it may be collected in a convenient pneumatic apparatus.

The acid obtained by this process has a yellow colour; but it may be rendered colourless by simply raising it to the boiling temperature in a retort, taking care to remove the receiver while the acid is boiling hot, to prevent the deutoxide of azote thus driven off, from being again absorbed as the acid cools. If common nitre has been employed, the nitric acid obtained is always mixed with some muriatic. Nor can nitre be quite freed from all traces of common salt, though repeatedly crys-But if we put the impure nitric acid into a retort, and distil off about one-third of it by rather a slow fire, the remaining two-thirds in the retort will be quite pure, all the muriatic acid having passed along with the acid distilled over. method, first proposed by Lassone and Cornette,\* I have been in the habit of following, and easily obtain by means of it pure nitric acid; while the portion distilled over answers all the numerous purposes to which a mixture of nitric and muriatic acids is usually applied.

Nitric acid thus prepared is a liquid colourless as water; but Properties if we expose it to the direct rays of the sun, or even to the light of day, it gives out oxygen gas, and soon assumes a yellow colour. It absorbs deutoxide of azote with avidity, and becomes first yellow, then red, and at last brown, and so volatile that a very moderate heat converts it wholly into vapour.

It has a peculiar smell, and gives out a white smoke when exposed to the air. Its taste is intensely sour, it reddens veges table bines, and corrodes and destroys animal and vegetable substances with great energy. Hence it is often applied by

surgeons to ill conditioned ulcers as a caustic, and when so applied it answers better, and gives less painwhen strong than when diluted with water.

Strength.

It has a strong affinity for water, and cannot be obtained free from that liquid. When the concentrated acid is exposed to the air, it absorbs moisture from the atmosphere. The following table shows the specific gravity of various atomic combinations of this acid with water.\*

Atoms of acid.	Atoms of water.	Acid in 100 parts.	Specific gravity.
1	1	85.714	1.55
1	2	75.000	1.4855
1	3	66.668	1.4546
1	4	60.000	1.4237
1	5	54.545	1.3928
1	6	50.000	1.3692
1	7	46.260	1.3456
1	8	42.857	1.3220
1	9	40.000	1.3032
1	10	37.500	1.2844
1	11	35.294	1.2656
1	12	32.574	1.2495
1	13	31.579	1.2334
1	14	30.000	1.2173
1	15	28.571	1.2012

The boiling temperature of this acid varies with its strength.

The following table drawn up by Mr. Dalton, from his own experiments, shows the temperature at which acid of different densities begins to boil.+

•				
Sp. gravity of acid.			:	Boiling point,
1.54	•	•	•	175
1.50	•	•	•	210
1.45	•	•	•	<b>240</b>
1.42		•	•	<b>248</b>
1.40	•	•	•	247
1.35		. (	•	<b>242</b>
1.30	•	•	•	236
1.26		•	•	232
1.22				229
1.20			•	226

<sup>\*</sup> First Principles, i. 114.

<sup>†</sup> New System of Chemical Philosophy, ii. 355.

Specific gravity of	gravity of acid. Boiling point.		Class I.		
1.18	•	•		223	Div. I.
1.17	•	•	•	<b>2</b> 21	
1.16	•	•	•	220	
1.15	•	•`•	•	219	
1.14	•	•	•	219	

We see from this table that the boiling point of acid of the specific gravity 1.42, or acid composed of 1 atom acid + 4 atoms water is a maximum or 248°. The boiling point of acid either stronger or weaker than this is lower.

The acid which occurs in commerce under the name of aquafortis or single nitric acid, is obtained by distilling a mixture of
nitre and sulphate of iron in cast-iron retorts luted to large green
glass receivers. It is colourless, or has only a very light shade of
yellow. The specific gravity of what is usually made in this
country is about 1.22, and it contains about 31 per cent. of real
acid. It rarely or never contains any iron; but is never free
from muriatic acid.

not act upon charcoal and sulphur unless the temperature be

If a piece of charcoal be ignited and thrown into

concentrated nitric acid it continues to burn with great violence, giving out red vapours. When boiled upon sulphur it gradually converts it into sulphuric acid. Phosphorus when thrown into concentrated nitric acid catches fire and burns with much splendour. On iron concentrated nitric acid does not act instantly, but if we elevate the temperature the action begins suddenly and becomes extremely violent; much heat being evolved, and even light it is said; though this has never happened in my trials. It acts also with great violence on zinc, tin, copper, and manganese. Mercury, silver, cadmium, bismuth, lead, cobalt, and nickel, are dissolved by it rapidly, and with effervescence. Upon gold, platinum, palladium, rhodium, iridium, and osmium, it either does not act at all or only very feebly. Concentrated nitric acid sets fire to various volatile

The combustion of oils by this acid was first taken notice

Most combustible substances decompose this acid; but it does Action on other bodies,

of by Borrichius and Slare;\* but it is probable that Homberg communicated it to Slare. In order to set fire to the fixed oils, it must be mixed with some sulphuric acid; the reason of which seems to be, that these oils contain water, which must be previ-

<sup>\*</sup> Phil. Trans. Abr. ii. 653, and iii. 663,

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ously removed. The sulphuric acid combines with this water, and allows the nitric acid, or rather the oil and nitric acid together, to act. The drying oils do not require any sulphuric acid: they have been boiled, and consequently deprived of all moisture.

Dilute nitric acid has the property of giving a yellow colour to vegetable and animal substances. In this way it dyes the cuticle, and the yellow colour becomes orange when washed with soap, and remains indelible till the stained portion of the cuticle be removed. It is employed to give a yellow border to the blue or green woollen cloth used in this country for covering tables. Many vegetable and animal substances when digested in it are converted into oxalic acid, malic acid, carbonic acid, suberic acid, wax, or fatty matter like tallow, and sometimes also into hydrocyanic acid.

It has the property of neutralizing bases, and forming a class of salts called nitrates.

Composition.

The first step to the knowledge of the constituents of this acid was made by Lavoisier, who proved by direct experiment, that it might be resolved into deutoxide of azote and oxygen gas; and that these two gases when placed in contact, immediately reunited and formed nitric acid. He concluded in consequence that nitric acid is a compound of deutoxide of azote and oxygen; and he even tried to determine the proportion of the two constituents, but the result obtained does not constitute a very near approximation to the truth.\* Mr. Cavendish showed that when azotic and oxygen gases are mixed, and electric sparks passed through the mixture in a glass tube standing over potash ley, the two gases unite together and form nitric acid, which gradually saturates the potash, and converts it into Hence it followed that the true constituents of this acid are azote and oxygen. From the proportions of the two gases which disappeared in this experiment, it appeared that nitric acid was a compound of

1 volume azotic gas,

2 volumes oxygen gas.

and with this the analytical experiments of Berthollet agreed.†
But it has been fully established by numerous experiments,
among others by several of my own,‡ that the true constituents
of this acid are

<sup>\*</sup> Mem. Par. 1776, p. 673.

<sup>†</sup> Mem. D'Arcueil, iii.

<sup>‡</sup> First Principles, i. 100.

1 volume azotic gas, 2½ volumes oxygen gas. l atom azote 1.75 or, 5 atoms oxygen 5 6.75

so that its atomic weight is 6.75.

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# 2. Hyponitrous Acid.

In the short account of hyponitrous acid which I have How obtained. given in the first volume of this work (p. 127), I have stated that it does not seem capable of existing except in combination with a base. However, M. Dulong has shown that this opinion He mixed together 4 volumes of deutis not well founded. oxide of azote, and I volume of oxygen gas, and exposed the mixture to the cold produced by a freezing mixture, it condensed into a deep green liquid, exceedingly volatile, and losing the liquid state when the cold was withdrawn. oxide of azote is a compound of equal volumes of azote and oxygen without any condensation whatever, it is evident that this green liquid was a compound of

2 volumes azotic gas,

3 volumes oxygen gas,

or (which is the same thing) of 1 volume azotic and  $1\frac{1}{2}$  volume oxygen gas. This is equivalent to

1 atom azote	•	•	1.75
3 atoms oxygen	•	•	3
			4.75

which is the composition of hyponitrous acid. Thus it appears from Dulong's experiment, that hyponitrous acid is capable of existing uncombined with a base.

This acid when in contact with air mixes with it and becomes a red vapour, which is not again condensible without the application of an intense cold. When this acid is mixed with water it undergoes a partial decomposition. Deutoxide of azote is given out with a strong effervescence, and there remains a solution of nitric and hyponitrous acid in the water. The same decomposition takes place when we attempt to combine thise acid with a base. But it is easy to obtain hyponitrites by double decomposition. The manner of proceeding is to boil a mixture of nitrate of lead and metallic lead in water; a dihyponitrite of lead is formed. If this hyponitrite be mixed with

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the requisite proportion of bisulphate, the oxide of lead and the sulphuric acid will unite and form an insoluble powder, while the hyponitrous acid will unite with the base to which the sulphuric acid was united, and form a hyponitrite which will dissolve in the water. We may also convert nitre into a hyponitrite by raising it to an incipient red heat, and keeping it for some time in that state. And several other nitrates may be converted into hyponitrites by a similar process.

Unites with other acids.

This acid has the curious property of combining with several other arids, especially with sulphuric acid. If we pass a mixture of four volumes deutoxide of azote and 1 volume of oxygen gas through concentrated sulphuric acid, we obtain a crystalline mass composed of sulphuric acid, hyponitrous acid, and water. When gently heated it melts, but becomes again solid on cooling. Its specific gravity is 1.831. When heated a little higher than 270° it undergoes decomposition, deutoxide of azote is disengaged, leaving a mixture of sulphuric and nitric acids. The nitric acid cannot be expelled by distillation, probably from want of water, without which that acid cannot exist in a separate state. When the crystalline mass is thrown into water deutoxide of azote is disengaged. When sulphurous acid, deutoxide of azote, and oxygen gas are mixed, the crystals do not appear unless water be at the same time present.

According to the analysis of Henry,\* this crystalline mass is composed of

4 atoms sulphuric acid	•	•	20
4 atoms water	•	•	4.5
1 atom hyponitrous acid	•	•	<b>4·75</b>
	*	-,	90.95

If we suppose the hyponitrous acid to unite with half of the sulphuric acid, the remainder will consist of 1 atom sulphuric acid united to two atoms water, which is the combination of that acid and water of most easy congelation. Is it to this that we are to ascribe the state of crystallization which the double acid assumes?

#### 3. Nitrous Acid.

In the first volume of this work (p. 128), I have given an account of the method of procuring nitrous acid from nitrate of lead, and likewise its properties and composition as determined by Dulong. What is called fuming nitric acid, contains a con-

<sup>\*</sup> Annals of Philosophy (2d series), xi. 368-

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siderable quantity of nitrous acid. If we distil such an acid by the heat of the water-bath into a receiver, kept cool by being surrounded with a mixture of snow and salt, and taking care to stop the distillation before the acid in the retort becomes colourless, what passes over is nitrous acid of a deep-red colour, and the air in the receiver is mixed with such a quantity of dense red fumes, that it appears quite opaque. Nitric acid dissolves it in considerable quantity, but only in fixed proportions. more than the requisite proportion be added, Mitcherlich has observed, that it separates from the acid, and swims on the surface as oil does on water. When this acid is mixed with water. deutoxide of azote is given out and nitric acid formed in it, and this goes on augmenting till at last it becomes altogether a combination of nitric acid and water. At least it becomes colourless by absorbing moisture from the atmosphere. evolution of deutoxide of azote is accompanied by a change of colour in the liquid. It passes from red to yellow, then to green, then to blue, and at last it becomes colourless.

Two different opinions have been advanced respecting the nature of *nitrous acid*. The greater number of chemists consider it as a peculiar acid, composed of

1 atom azote 4 atoms oxygen	•	•	1·75 4
•			E-75

But it is destitute of the property of combining with bases; no such class of salts as *nitrites* existing. On this account Berzelius considers it as a compound of

1 atom nitric acid	•	•	6.75
l atom hyponitrous acid	•	•	4.75
			11.50

And has given it the name of acidum nitrosonitricum. It is obvious that this view of its composition will come to the same thing, as far as the ultimate elements are concerned. For nitric acid being a compound of 1 atom azote and 5 atoms oxygen, and hyponitrous acid of 1 atom azote and 3 atoms oxygen, it is clear that if we combine them together we have a compound containing

2 atoms azote	•	•	3.5
8 atoms oxygen	.•	•	8

Chap. I. Now this is just the same as

1 atom azote	•	•	1.75
4 atoms oxygen	•	•	4
			5.75

which is the composition deduced from the analysis of Dulong. As nitrous acid does not combine with bases, it is a matter of indifference which of these views we adopt.

SECTION IV. -- OF THE ACIDS OF CARBON.

There are two acids at present known, composed of carbon and oxygen, namely, carbonic acid and oxalic acid.

#### 1. Carbonic Acid.

Carbonic acid exists ready formed in prodigious quantity in the mineral kingdom, constituting an essential constituent of carbonate of lime, which, under the names of marble, limestone, and chalk, occurs so abundantly in almost every part of the earth. It exists also in great abundance in carbonate of iron; while carbonate of barytes, strontian, magnesia, lead, copper, bismuth, and zinc, occur also in greater or smaller quantity in the mineral kingdom. It is given out also in great abundance by active volcanoes, and many springs in different parts of the earth are impregnated with it. It is formed also abundantly by the burning of wood and pit coal, and by the breathing of animals.

History.

The existence of this substance as an essential constituent of limestone, was first demonstrated by Dr. Black, who gave to carbonic acid the name of fixed air, because it exists in a fixed state in these mineral bodies. Its properties were first investigated by Mr. Cavendish. Mr. Keir, from a knowledge of these, first concluded that it was an acid, and gave it the name of calcareous acid. Bergman adopted the same opinion in 1774, and gave it the name of aerial acid.\* Mr. Bewdly called it mephitic acid, because it cannot be respired without occasioning death. Finally, Lavoisier, after proving it to be a compound of carbon and oxygen, gave it the name of carbonic acid, which has been long in universal use.

I have already given an account of the properties of this acid in the first volume of this work (p. 161). The salts which it forms with bases have received the name of carbonates. It is by no means a powerful acid, being expelled by the greater

number of the oxygen acids. As is the case with weak acids it has the property of uniting with the different bases in two, and frequently in three proportions.

This acid has been shown to be a compound of

1 atom carbon 0.752.00 2 atoms oxygen 2.75

and its atomic weight is 2.75.

# 2. Oxalic Acid.

As the earliest and best account of the oxalic acid was pub-Discovery. lished by Bergman, he was for a long time reckoned the discoverer of it; but Mr. Ehrhart, one of Scheele's intimate friends, informs us, that the world is indebted for its knowledge of this acid to that illustrious chemist,\* and Hermbstadt and Westrumb assign the discovery to the same author.+ The assertions of these gentlemen, who had the best opportunity of obtaining accurate information, are certainly sufficient to establish the fact, that Scheele was the real discoverer of oxalic acid.

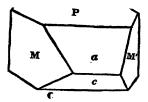
This acid exists, ready formed, in the vegetable kingdom, sometimes in the state of binoxalate of potash, as in oxalis acetosella and common sorrel; and sometimes in the state of oxalate of lime, as in the root of rhubarb and of many other plants. I have given a short account in the first volume of this work (p. 172), of the methods of preparing this acid. It may be procured also from the binoxalate of potash, by dissolving the salt in hot water, and adding carbonate of potash as long as any effervescence takes place. Then add a solution of acetate of lead, as long as a white precipitate continues to fall. lect the precipitate, wash it and dry it. For every 181 parts of this powder add 6.125 parts of strong sulphuric acid, previously diluted with ten times its weight of water, and digest the mixture for some time. The sulphuric acid will unite with the oxide of lead and form an insoluble powder, while the oxalic acid being disengaged will remain in solution. Separate the sulphate of lead, and concentrate the solution till the oxalic acid crystallizes.

Oxalic acid thus obtained is in transparent or translucent Properties. crystals, which have usually the form of flat tables, consisting in reality of six-sided irregular prisms. Mr. Brooke has shown

<sup>\*</sup> Elwert's Magazine for Apothecaries, 1785, part i. p. 54.

<sup>+</sup> Keir's Dictionary

that the primary form is an oblique four-sided prism. The figure in the margin represents the most common figure of the crystals, in which P, M, Mérepresent the primary faces. The following are the measurements of the angles made by Mr. Brooke.\*\*



•	•	98°	<b>30</b> ′
•	•	63	5
•	•	129	<b>20</b>
•	•	103	15
	•	•	63 . 129

The taste of these crystals is intensely sour, and when taken internally, even in very small quantity, they act as a poison. When taken to the amount of about half an ounce they act with great rapidity, and destroy life in a very short time; when given to the amount of half a drachm, they prove equally fatal; but not till after an interval of some days, as has been shewn by the experiments of Dr. Christison of Edinburgh. These crystals are soluble in about their own weight of boiling water: water at the temperature of 65.7° dissolves half its weight of them. The specific gravity of the solution is 1.0593.† One hundred parts of boiling alcohol dissolve 56 parts of these crystals; but at a mean temperature only 40 parts.‡ Liquid oxalic acid has a very acrid taste when it is concentrated, but a very agreeable acid taste when sufficiently diluted with water.

These crystals are composed of real oxalic acid and water. When heat is applied a portion of the acid is driven off, but not the whole. In several crystals of oxalic acid which I examined, exactly half the weight was water. Now as the atomic weight of this acid is 4.5, it is obvious that these crystals were composed of

1 atom acid	•	•	4.5
4 atoms water	•	•	. 4.5
			9

But from the experiments of Berzelius, Dr. Prout, and several other persons who have turned their attention to the subject, it would appear that in general they are composed of

1 atom acid	• •	•	<b>4·5</b>	
3 atoms water	•	•	3.375	
			-	
			7.875	
Philosophy (2d series)	). vi. 13	9.	+ Bergma	n. i.

<sup>\*\*</sup> Annals of Philosophy (2d series), vi. 119. ... † Ibid.

Bergman, i. 255.

<sup>§</sup> Ibid.

or that they contain one atom less water than the crystals which I examined. When we heat these crystals we can drive off two atoms of the water. But the third atom remains, and cannot be got rid of unless we combine the acid to a base. when we unite it to lime, the oxalate of lime formed still retains the atom of water.

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Oxalic acid is a much more powerful acid than carbonic; yet it has a tendency like it to combine with bases in two or three proportions. The salts which it forms are called oxalates. Though it is composed, like carbonic acid, of carbon and oxygen, constitution, yet the state of the constituents in it must be different from their state in carbonic acid. When a carbonate is heated, the carbonic acid either remains fixed to the base, or it is driven off unaltered. But when an oxalate is heated, the acid undergoes decomposition. Carbonic acid and carbonic oxide are usually driven off, and frequently a quantity of charcoal is evolved. No oil is ever given out, as happens when acids with a compound base are distilled. In short, oxalic acid bears a striking analogy to acids with a compound base, though it contains only carbon and oxygen. Dulong has endeavoured to account for this anomaly by considering the atom of water that cannot be driven off by heat, as an essential constituent of the acid. According to this view of its constitution it would be a compound of

4 atoms oxygen	•	•	4
2 atoms carbon	•	•	1.5
1 atom hydrogen	•	•	0.125
			5.695

But the objection to this view of the acid is, that it may be united to some bases, as oxide of lead and oxide of zinc, without the atom of water, which seems essential to its existence in an isolated state. Then its atomic weight is 4.5, and it consists of

3 atoms oxygen	•	•	3
2 atoms carbon	•	•	1.5
			4.5

The fact that it is a more powerful acid than carbonic, though it contains less oxygen, is inexplicable, unless we view it as an acid with a compound base. For in them the strength of the acid is undoubtedly dependant upon something else than the preponderancy of the electro-negative constituent, which undoubtedly produces the effect in acids with a simple base.

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#### SECTION V .- ACIDS OF BORON AND SILICON.

The acids formed by the combination of these two bases with oxygen, are two in number. They are both feeble acids, and capable of combining with bases in various proportions.

### 1. Boracic Acid.

This acid united to soda occurs in China and Thibet. It occurs in a free state, and seemingly in great abundance in several lakes in Tuscany. Great quantities of this native acid have for some time been imported into this country, where it is converted into borax for the use of the potters, who have been long in the habit of using it as a glaze for the finer kinds of stone-ware. The most considerable of the Tuscan lakes which yield this acid is the Cerchiajo, on the Monte rotondo. Though it is only about 60 feet long and 42 feet broad, the soil in the neighbourhood becomes covered with an efflorescence consisting chiefly of boracic acid, but mixed with sal ammoniac, and some other saline matters.

Preparation.

Boracic acid is usually prepared from borax. Four parts of this salt are dissolved in boiling water, and one part of concentrated sulphuric acid is added to the solution. The boracic acid is deposited in crystalline scales as the liquid cools. These scales are to be collected, dried, and then exposed to a red heat in a platinum crucible to drive off a portion of sulphuric acid, which cannot be separated by washing. It may then be dissolved in boiling water and crystallized anew.

Properties.

Boracic acid, thus procured, is in the form of thin hexagonal scales, of a silvery whiteness, having some resemblance to spermaceti, and the same kind of greasy feel. It has a bitterish cooling taste, and at last leaves an agreeable sweetness. It has no smell; but when sulphuric acid is poured on it, a transient odour of musk is produced.\*

It reddens vegetable blues feebly. And Mr. Faraday has likewise remarked that it reddens turmeric paper. Its specific gravity, while in scales, is 1.439,† but after ignition it becomes as high as 1.830.‡

It is not altered by light. It is fixed in the fire. At a red heat it melts, and is converted into a hard transparent glass; which becomes somewhat opaque when exposed to the air, but does not attract moisture.

<sup>\*</sup> Reuss, de Sale Sedat. 1778. † Kirwan's Mineralogy, ii. 4.

<sup>‡</sup> Roget and Dumas, Annals of Philosophy (2d series), iii. 392.

I have already stated that the atomic weight of boracic acid Class L Div. L is 3, and that it is a compound of

1 atom boron 2 atoms oxygen . 3

The scales obtained constitute a hydrated acid composed of

1 atom acid. 2 atoms water 5.25

It is very sparingly soluble in water. Boiling water scarcely dissolves 0.02 of boracic acid, and cold water a still smaller quantity. When this solution is distilled in close vessels, part of the acid evaporates along with the water, and crystallizes in the receiver. Water, therefore, renders it in some measure volatile, though it is perfectly fixed when in a state of dryness.

It is soluble in alcohol; and alcohol containing it burns with a green flame. Paper dipped into a solution of boracic acid burns with a green flame.

With the assistance of a distilling heat, it dissolves in oils, especially in mineral oils; and with these it yields fluid and solid products, which give a green colour to spirit of wine.

Boracic acid is an exceedingly feeble acid; so much so that it is capable of acting on very few of the metals. we except iron and zinc, there are none of these bodies which it is capable of dissolving. It combines with bases in a great variety of proportions; but no quantity of it whatever is capable of depriving potash or soda of the property of giving a green colour to vegetable blues.

The salts which it forms have received the name of borates. Their properties have not been much investigated.

#### 2. Silicic Acid.

Silica, or silicic acid, as it should be called, exists in greater abundance than any other, as it enters as a constituent into most of the rocks and stony bodies of which the earth is composed. There are no fewer than 167 species of minerals that contain silica as one of their essential constituents. Rock crystal, quartz, chalcedony, and flint consist of silica very nearly, but not quite in a state of purity. But from these bodies it is easy to obtain it quite pure by the following process: Put into a platinum Preparation. crucible equal weights of anhydrous carbonates of potash and

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soda which enter into fusion at a comparatively low temperature, and to the liquid mass add a quantity of flint or quartz, previously reduced to a fine powder. Carbonic acid gas will be given out, and the powder will dissolve in the alkaline liquid. Continue to add the powder as long as the effervescence continues. Then allow the whole to cool, and dissolve it in dilute muriatic acid, which will dissolve both the alkali and the silica. Filter the solution and concentrate it by evaporation. It will assume the form of a thick transparent jelly. Continue the heat till the jelly becomes a dry powder, and digest this powder for a couple of hours in concentrated muriatic acid. Then add a sufficient quantity of hot water, and throw the whole upon a filter. Wash the silica perfectly, and then allow it to dry. Finally expose it to a red heat to expel all the water which it may retain.

Properties.

Silica, thus obtained, is a fine white powder, without either taste or smell. Its particles have a harsh feel, as if they consisted of very minute grains of sand. Its specific gravity is 2.66.\*

It may be subjected to a very violent heat without undergoing any change. Lavoisier and Morveau exposed it to the action of a fire maintained by oxygen gas without any alteration.† Saussure succeeded in fusing, by means of the blow-pipe, a portion of it so extremely minute as scarcely to be perceptible without a glass. There is no difficulty in fusing it by means of the oxygen and hydrogen plow-pipe.

When silica is precipitated from fluosilicic acid gas by water, it dissolves very readily, and in considerable quantity, in that liquid. But after ignition it loses its solubility entirely. When boiled in a solution of carbonate of potash, or carbonate of soda, it dissolves in considerable quantity, and the solution, if concentrated, gelatinizes on cooling. But if we dilute it with boiling water, the silica remains in solution after the liquid has become cold. Yet no carbonic acid is given off in this case. This method of dissolving silica in an alkaline carbonate was first observed by Pfaff. It is in this way that it is held in solution by the Geyser springs in Iceland.

Most springs of water contain a small quantity of silica in solution. The only acid which dissolves it after ignition is the fluoric. This property enables us to apply fluor spar with great advantage to the analysis of minerals. If we mix a mineral to be analyzed (previously reduced to fine powder) with fluor spar and sulphuric acid, and heat the mixture, the whole silica will

<sup>\*</sup> Kirwan's Min. i. 10. † Jour. de l'Ecole Polytech. l. iii. 299.

escape in combination with the fluoric acid; and the alkali, if any be present, may be obtained in the state of sulphate by digesting the residual matter with water.

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Silica has the property of combining in definite proportions Hydrates. with water. But the compound is not very intimate. Yet that an affinity exists between silica and water is obvious from the gelatinous state which it assumes. Gelatinous silica allowed to dry in the open air till it ceases to wet paper, though still retaining its state, is a compound of

When the jelly is allowed to dry in the open air it assumes the appearance of gum arabic, or indeed of chalcedony (only it wants the hardness of that mineral). In that state it is a compound of

> 1 atom silica . . 2 1 atom water . . 1·125 3·125

When silica is fused with an alkaline carbonate, if we dissolve the mass in a small quantity of water, light white flocks of silica remain. When these flocks are washed and dried in a temperature of about 85°, they constitute a dihydrate composed of

2 atoms silica . . 4
1 atom water . . 1·125
5·125\*

Though silica does not redden vegetable blues, yet it enters into definite compounds with the different bases, and forms saline compounds which are distinguished by the name of silicates. Like other weak acids, it is capable of entering into a great variety of combinations with bases. The compounds which it forms are frequently so intimate, that no other acid is capable of removing the base and setting the silica at liberty. The different kinds of glass consist of two or more silicates melted together. Silicates of potash and of soda are soluble in water, but when a little of an earthy silicate is added the glass becomes insoluble.

I have shown in the first volume of this work (p. 225), that the atomic weight of silica is 2, and that it is a compound of

<sup>\*</sup> First Principles, i. 191.

SECTION VI. -- OF THE ACIDS OF PHOSPHORUS.

Phosphorus combines in various proportions with oxygen, and forms at least four acids, of which I shall treat in the present section.

# 1. Phosphoric Acid.

This acid exists chiefly in the animal kingdom, where united to lime it constitutes about  $\frac{5}{6}$ ths of the earth of bones. It occurs also in the mineral kingdom, constituting 13 mineral species in which this acid occurs united to different bases, as lime, magnesia, alumina, oxides of iron, copper, uranium, &c.

Preparation.

It is usually procured from earth of bones, and I have given one of the easiest processes in the first volume of this work (p. 237). We may obtain the acid likewise by burning phosphorus in a porcelain cup, and covering it with a glass jar capable of holding about 300 cubic inches. The phosphorus burns with splendour, and a white smoke rises which condenses upon the inside of the glass like flakes of snow. This combustion may be repeated (taking care to renew the air of the jar every time), till we obtain enough of phosphoric acid for the object in view.

Another method (first put in practice by Lavoisier), is to dissolve phosphorus by boiling it gently in a retort with twelve times its weight of strong nitric acid, previously diluted with twice its weight of water. The solution goes on with effer-vescence, deutoxide of azote being evolved. A receiver should be attached to the retort, and after the phosphorus is dissolved the nitric acid should be gently distilled off, till the acid in the retort acquires the thickness of a syrup. It is now to be put into a platinum crucible and gradually raised to a red heat. It gives out water, and melts into an oily looking liquid, and by continuing the heat it becomes at last a transparent, colourless liquid like water, which, on cooling, assumes the appearance of perfectly limpid glass. In this state I found it a compound of

Hydrates.

5.625

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It was therefore a hydrate of phosphoric acid. By continuing the heat more of the water may be driven off. Dulong obtained it composed of almost exactly one atom of acid and one atom of water as I did, but M. H. Rose, by continuing the heat longer, reduced the water so much, that what remained was a compound of

Phosphoric acid . . . 4.5
Water . . . 0.469

Now 0.469 of water is not much more than  $\frac{1}{3}$  of an atom. Rose, therefore, had obtained nearly a trishydrate, or compound of

3 atoms acid . . . 13.5 1 atom water . . . 1.125

14.625

But however long continued the heat may be, we cannot drive off the whole of the water.

Though the volatility of this acid be inconsiderable, yet at a red heat it rises in a white smoke, and might probably be dissipated, were the heat long enough continued. With the vapour of water it volatilizes very perceptibly.

The specific gravity of this acid, in a state of dryness, is 2.687;\* in the state of glass, 2.8516;† in the state of deliquescence, 1.417.‡

This acid is very soluble in water. When in the state of white flakes, it dissolves with a hissing noise, similar to that made by red-hot iron plunged into water. When in the state of glass it dissolves much more slowly. The heat evolved during the combination of this acid and water is much inferior to that evolved when sulphuric acid enters into a similar combination. Phosphoric acid obtained by deliquescence, when mixed with an equal quantity of distilled water, acquired so little heat as to raise the thermometer only one degree, as Mr. Sage observed. M. Lavoisier raised the thermometer from 50° to 63° by mixing phosphoric acid, boiled to the consistence of a syrup, with an equal quantity of water; and from 50° to 104° when the acid was as thick as turpentine. When the flocks of this acid have been ignited, they resist solution in water for a considerable time, and float about in it not unlike flocks of

<sup>\*</sup> Bergman's Sciographia, p. 20. Eng. Trans.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 11.

<sup>‡</sup> Encyc. Method. Chim. i. 221.

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silica. Yet they at last disappear, and constitute a limpid solution, provided the phosphoric acid be quite disengaged from a base.

Though this acid acts with but little energy upon animal and vegetable substances, it combines readily with bases, and forms a class of salts called *phosphates*. Its tendency to unite with these bases is very energetic, and when assisted by heat it is capable of driving off all acids which possess volatility, even sulphuric, nitric, and muriatic, which have a stronger affinity than it for bases by the moist way. It has the property of uniting with most bases in a variety of proportions, and the alkaline phosphates crystallize most readily when they contain two atoms of acid united to one atom of base.

When dropt into a solution of nitrate of silver, a yellow precipitate falls, which is a subsalt. This tendency which it has to form subsalts, makes it very difficult to analyze the phosphates by precipitation. We can dissolve iron and zinc in dilute phosphoric acid, but scarcely any of the other metals. The phosphates are best obtained by double decomposition. A great number of them are insoluble in water; but they all dissolve in nitric and muriatic acids.

I have shown in the first volume of this work (p. 238), that phosphoric acid is a compound of

1	atom phosphorus	•	•	· 2
$2\frac{1}{2}$	atoms oxygen	•	•	2.5
				4.5

### 2. Pyrophosphoric Acid.

Discovery.

In the year 1827, Mr. Thomas Clark of Glasgow, observed, that when the common phosphate of soda of the shops was exposed to a red heat, its nature was altered. When the ignited salt was dissolved in water and crystallized, the shape of the crystals was quite different from that of common phosphate; it contained only half as much water of crystallization, and it was not the least altered by exposure to the air, whereas common phosphate of soda speedily effloresces. When a solution of this new salt was dropt into nitrate of silver, a white precipitate fell consisting of neutral phosphate of silver, whereas common phosphate of soda throws down a yellow-coloured subsalt. Mr. Clark gave to his new salt the name of pyrophosphate of soda, and to the acid which it contains, and which

obviously possesses different properties from those of common phosphoric acid, the name of pyrophosphoric acid.\*

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M. Stromeyer of Gottingen informs us that one of his pupils had some years ago made a similar observation with Mr. Clark, that ignited phosphate of soda precipitated silver white. Stromeyer himself had ascertained that phosphoric acid prepared by means of nitric acid from phosphorus, acquired the same properties by ignition, and that phosphoric acid prepared by burning phosphorus possesses it also. Stromeyer resumed his investigation of the subject after the publication of Mr. Clark's paper, and ascertained that the characters and composition of the phosphate and pyrophosphate of silver are quite different. He found that when pyrophosphate of silver and phosphate of soda are boiled together a double decomposition takes place, and there are formed phosphate of silver and pyrophosphate of soda. All the other pyrophosphates tried were equally decomposed by phosphate of soda. He found also that when nitrate of silver was dropt into a mixture of phosphate and pyrophosphate of soda, phosphate of silver precipitates first and afterwards pyrophosphate of silver. It is obvious from this that pyrophosphoric acid is a weaker acid than phosphoric. The pyrophosphates of lead, copper, nickel, cobalt, uranium, bismuth, manganese, mercury, glucina, and yttria, are redissolved with great facility by an excess of pyrophosphate of While the precipitates produced by phosphate of soda are not redissolved by an excess of that salt, this shows very clearly that the pyrophosphates have a much greater tendency to form double salts than the phosphates.+

It is clear from all this that pyrophosphoric and phosphoric acids possess quite distinct characters. But Stromeyer has shown that the proportion of the elements of both is exactly the same, each being a compound of

1 atom phosphorus	•	•	2
$2\frac{1}{2}$ atoms oxygen	•	•	2.5
	•		
			4.5

I was induced at the request of Mr. Clark to examine the constitution of his pyrophosphoric acid at the time of his discovery, and I was surprised to find that its atomic weight was precisely the same as that of common phosphoric acid. To what then are we to ascribe the difference between these two acids? The

<sup>\*</sup> Brewster's Edin. Journal, vii. 298.

<sup>†</sup> Ann. de Chim. et de Phys. xliii. 364.

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atoms of which they are composed amount to  $3\frac{1}{2}$ ; or if we think it necessary to get rid of the half atom, by doubling the number of atoms then the atoms will amount to 7, of which 2 are phosphorus and 5 oxygen. Now it is perfectly conceivable that 7 atoms may arrange themselves two different ways, and that when in one arrangement they may form phosphoric acid, and when in another pyrophosphoric acid. We shall find as we proceed that these two acids are not the only ones whose atomic constitution is the same. There are several others in exactly the same circumstances, and doubtless new ones will come under our review, as the science of chemistry continues to advance.

It is evident from the analyses of Stromeyer, that the pyrophosphate of silver is a compound of

1 atom acid . . . . 4.5
1 atom oxide of silver . . . 14.75
while the yellow phosphate is a compound of
1 atom acid . . . . 4.5

All the salts of the pyrophosphoric acid seem to be neutral, while many of the phosphates have an excess of base or of acid.

### 3. Phosphorous Acid.

The mode of forming this acid by means of sesquichloride of phosphorus first employed by Sir H. Davy, has been given in the first volume of this work (p. 239). It may be obtained in an anhydrous state, or nearly so by burning phosphorus in a glass tube, drawn out at one extremity into a capillary orifice. The phosphorus when heated sufficiently burns with a greenish flame, and gives out but little light, and the phosphorous acid formed is condensed in the inside of the tube in the state of a white powder. In this state it is volatile, and may be driven by the heat of a lamp from one part of the tube to another. When brought into the open air it catches fire and burns with splendour, being converted into phosphoric acid; but if we allow it to remain in the tube it gradually absorbs moisture, and is converted into a liquid.

Preparation.

According to Droquet the easiest method of obtaining this acid is to put a quantity of phosphorus into the bottom of a glass cylinder, with a narrow orifice filled with hot water, and by means of a glass tube to cause a current of chlorine gas pass through the liquid phosphorus. It is instantly absorbed. The process is to be continued till the chlorine gas begins to disen-

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gage itself from the phosphorus, when we must stop, otherwise phosphoric acid would be formed. Sesquichloride of phosphorus is formed and decomposed by the water into muriatic acid and phosphorous acid. When the whole has become cool the liquid portion is decanted off, and the muriatic acid is separated by distilling it in a retort till it becomes of a syrupy consistence. If we now put it under the exhausted receiver of an air-pump, together with pieces of solid potash to absorb the water, and any muriatic acid that may be evolved, the phosphorous acid gradually shoots into transparent prismatic crystals.

Davy ascertained that ten parts of it when heated in close composition. vessels left 8.5 parts of phosphoric acid, and gave off 1.5 parts of sesquihydret of phosphorus.\* This would make the crystals

to be composed of nearly

4 atoms phosphorous acid,  $1\frac{1}{2}$  atom of water.

But the experiment could not be correct, because the phosphoric acid would retain a certain quantity of water.

Phosphorous acid has an acid taste, and reddens vegetable blues. It is obviously a very feeble acid. When exposed to the air it absorbs oxygen, and is converted into phosphoric acid; but this change goes on very slowly if the acid be concentrated. It is much more rapid when the acid is diluted with water. When we mix it with oxides or salts that easily part with oxygen, as for example with oxide of mercury, it is instantly converted into phosphoric acid, and the oxide is reduced to the metallic state. If we attempt to dissolve iron or zinc in this acid, sesquihydret of phosphorus is given out, and a phosphate of the iron or zinc formed.

We might represent phosphorous acid as a compound of

3 atoms phosphoric acid,

2 atoms phosphorus.

For 3 atoms phosphoric acid are composed of

3 atoms phosphorus,

 $7^{1}_{\sigma}$  atoms oxygen.

If to this we add 2 atoms of phosphorus, we have a compound of

5 atoms phosphorus,

 $7\frac{1}{2}$  atoms oxygen.

Now this is the same thing as

\* Phil. Trans. 1812, p. 408.

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1 atom phosphorus	•	•	2 1·5
1½ atom oxygen	•	•	
			2.5

which has been shown (Vol. I. p. 239) to be the constitution of this acid. When heat is applied the two additional atoms of phosphorus are separated, and coming in contact with the water chemically united to the acid they decompose it, and are converted into phosphuretted hydrogen and phosphoric acid.

When phosphorus is allowed to undergo slow combustion by exposure to the atmosphere, it runs into a liquid having the smell of garlic, and an exceedingly sour taste. This liquid was considered by chemists as pure pliosphorous acid, till Dulong and Thenard showed that during the process it was partly converted into phosphoric acid. According to the experiments of Dulong, this acid, to which he gave the name of phosphatic acid, is a compound of

100 parts phosphorus,109 parts oxygen.

This comes very nearly to

2 atoms phosphoric acid, 1 atom phosphorous acid.

But there cannot be the least doubt that the proportions of these acids vary exceedingly according to the temperature and the state of the atmosphere when the acid is formed. It cannot, therefore, be considered as any thing else than a mixture of the two acids in various proportions according to circumstances which cannot easily be appreciated.

## 4. Hypophosphorous Acid.

I have given an account of the formation and constitution of this acid in the first volume of this work (p. 240). M. H. Rose has shown that it is a compound of

2 atoms phosphorus	•	•	4
1 atom oxygen	•	•	1
			5

It is therefore quite similar in its composition to the hyposulphurous acid of Herschel. Its taste is sharp and very sour. It combines with the different bases, and forms salts to which the name of *hypophosphites* has been given. They are distinguished by their great solubility in water. Not one having been yet examined which does not possess this property, while many of the phosphates and phosphites are insoluble.

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#### SECTION VII. -- ACIDS OF SULPHUR.

Sulphur and oxygen combine in a great variety of proportions, and form no fewer than 5 acids, some of which are of great importance both to the chemist and the manufacturer.

### 1. Sulphuric Acid.

This acid, which is upon the whole the most essential of the History. whole tribe, appears to have been known to Geber as early as the 7th century. For the first great improvement in the method of manufacturing it we are indebted to Dr. Roebuck, whose establishment in Prestonpans in Scotland was not broken up till about the year 1820. Prodigious improvements have been introduced into the method of making sulphuric acid since the commencement of the present century, and the price has been reduced from ninepence per pound to less than three halfpence, while the quality has been rather improved.

There are two different methods of making it in use among Nordhausen process. manufacturers. The first which is practised at Nordhausen in Germany yields a dark-coloured fuming acid, which is chiefly used for dissolving indigo for the Saxon dye. In this manufactory it is prepared from sulphate of iron. It is heated in a calcining furnace, which expels most of the water of crystallization, and at the same time peroxidizes the iron which it con-It is then put into stoneware retorts, and exposed to a heat gradually raised nearly to whiteness. The acid leaves the oxide of iron and passes into the receiver in combination with the small quantity of water which the calcined vitriol retained. Acid prepared in this way is known by the name of fuming acid of Nordhausen.

The process followed in Great Britain, and which has been British process, adopted in most other countries, is much more economical; but the acid which it furnishes contains a greater quantity of water. Large chambers are erected lined with sheet-lead, about 70 feet long, 20 wide, and as much in height. At one end of these chambers is a kind of hearth, the chimney of which communicates with the chamber. On this hearth the sulphur from which the sulphuric acid is made is put and kindled. very ingenious contrivance a strong draft of air is made to pass over this hearth into the chamber, so that the sulphur burns briskly, and is converted into sulphurous acid, which passes

into the leaden chamber. Upon the burning sulphur is placed an iron basin, containing a quantity of saltpetre, mixed with the requisite quantity of sulphuric acid to produce complete decomposition. The heat of the burning sulphur is sufficient to heat this mixture sufficiently high to drive off the nitric acid in vapour, which passes into the leaden chamber mixed with the sulphurous acid. The bottom of the leaden chamber is covered with water to the depth of about 4 inches. sequence of this is that the air of the chamber always contains a quantity of vapour of water. The nitric acid fumes speedily convert a portion of the sulphurous acid into sulphuric acid, which falling by its weight into the water, at the bottom deutoxide of azote is disengaged in the gaseous form. It speedily unites to an atom of oxygen, and is converted into hyponitrous acid. Now when hyponitrous acid, sulphurous acid, and vapour of water, meet together, they unite and form a crystalline body, having considerable resemblance to glauber salt in its appearance. This saline matter is probably a compound of

> 1 atom sulphurous acid, 1 atom hyponitrous acid, 1 atom water.

When it comes in contact with water, the hyponitrous acid parts with an atom of oxygen to the sulphurous acid, and converts it into sulphuric acid, while the deutoxide of azoteinto which it is converted makes its escape in the gaseous state, and when it comes into the atmosphere it is again converted into hyponitrous acid by combining with an atom of oxygen. It again unites with sulphurous acid and water; and thus the process goes on till the whole sulphurous acid is converted into sulphuric acid.

This process continues till the water at the bottom of the leaden chamber has become impregnated with as much sulphuric acid as it can take up. Its specific gravity is now 1.75. To concentrate it farther it was the custom to put it into glass retorts, which were exposed to a heat of above 600°. The water passed over along with a considerable quantity of acid, and the sulphuric acid remaining in the retort, was as much concentrated as it could be by simple distillation. But of late years large cylindrical stills of platinum, furnished with platinum heads, have been introduced, which is found to answer much better; because the retorts, when exposed to so high a temperature, were very apt to be broken, to the great injury of the manufacturer. Formerly the acid was taken from the

chambers before it had reached the specific gravity of 1.75, and was concentrated in large leaden boilers. This occasioned the presence of a little sulphate of lead in the acid, which is now avoided by the present process.

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One of the largest manufactories of sulphuric acid in this country is that of Charles Tennant and Co. at St. Rollock, near Glasgow, where about 200,000 lbs. of the acid are made weekly. This prodigious quantity of acid (and there are many other makers) is all consumed by the bleachers and chemical manufacturers of Great, Britain. Very little of the acid is exported.

The sulphur from which this acid is made is imported from Sicily, where it occurs in immense quantity in a formation which seems to be newer than the secondary rocks, though there is no evidence that it is volcanic. Sicily furnishes sulphur of various degrees of purity; and the sulphuric acid makers prefer the second quality to the first, because it burns better.

When the fuming acid of Nordhausen is put into a glass retort, and distilled by a moderate heat (the receiver being surrounded with ice), the fuming portion comes over first, and may be obtained in a separate state by stopping the distillation in time. Thus obtained, it constitutes sulphuric acid in a state of absolute purity.

In this state it is solid, and appears as if it were composed How obtain-of silky filaments. It is tough and difficult to cut, and bears considerable resemblance to the mineral called asbestos. When exposed to the air, it fumes strongly, and gradually flies off in vapour. It may be held for some time between the fingers without any sensible action on the skin; but, after a certain time, a sensation of pain is perceived in the interior of the fingers. It remains solid at a temperature at least as high as 66°; but when the heat is increased, it assumes the form of a colourless vapour, which becomes white when it comes in contact with moist air. I have sometimes obtained it in transparent rhombic crystals, differing very little from a right angle. In such cases it had combined with a certain quantity of water: but much less than exists in the fuming acid.

The solid acid becomes liquid, according to Bussy, when Properties. heated up to 64°, and at the temperature of 68° its specific gravity is 1.97. It is rather hazardous to liquefy this acid, because it is converted into a gas at a temperature not much higher than its point of liquefaction. The specific gravity of this vapour is doubtless 2.7777, since it is a compound of 1 volume of

sulphurous acid and half a volume of oxygen gas condensed into 1 volume.

When dropped into water, it combines with that liquid so violently as to make a noise similar to that made by a red-hot bar of iron when dipped into water. When the quantity of acid is considerable, a kind of explosion takes place, owing to the suddenness with which a great deal of heat is evolved; but nothing is extricated except water in the state of vapour. When united with about one-fifth part of its weight of water, it is converted into the common concentrated sulphuric acid of commerce, which is a hydrate of sulphuric acid.

From the experiments of Vogel, it appears that absolute sulphuric acid is capable of dissolving sulphur, and of assuming a blue, green, or brown colour, according to the proportion of sulphur held in solution. Phosphorus decomposes it, and absorbs its oxygen with such impetuosity as to take fire.\*

The specific gravity of Nordhausen acid is 1.896. When as strong as possible it is a compound of

2 atoms sulphuric ac	eid	•	•	10
1 atom water	•	•	•	1.125
				11.125

But it most generally contains more water than this. The weakest acid that I have had an opportunity of examining was a compound of

4 atoms acid . . . 20 . 3 atoms water . . . 3.375

Such acid when heated gives out rather less than  $\frac{1}{4}$ th of its weight of solid acid. The weaker the Nordhausen acid is, the higher is the temperature at which it freezes. I have had it capable of congealing at a heat of  $42^{\circ}$ .

Hydrous acid.

The concentrated acid of this country is a transparent liquid, like water, and having somewhat of an oily consistency. Hence the old name of oil of vitriol, by which it was distinguished. Its taste is intensely acid. It reddens vegetable blues, and speedily chars those animal and vegetable substances to which it is applied, especially if its action be assisted by heat. Its specific gravity when in a state of purity, and as much concentrated as possible, I find to be 1.84238. When it is higher than this it contains some foreign salt in solution.

Its specific gravity, and its boiling point, vary according to

the proportion of water which it contains. The following very valuable table, drawn up by Mr. Dalton, from his own experiments, exhibits a satisfactory view of both of these variations.\*

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Strength and boiling points.

Acid.	Atom	s. Vater.	Acid per cent. by weight.	Acid per cent. by measure.	Specific gra- vity.	Boiling point,
1	+ l		81	150	1.850	620°
-	•		80	148	1.849	605
			79	146	1.848	590
			78	144	1.847	575
			77	142	1.845	560
1			76	140	1.842	545
			75	138	1.838	530
l			74	135	1.833	515
			73	133	1.827	501
			72	131	1.819	487
			71	129	1.810	473
			70	126	1.801	460
			69	124	1.791	447
1	+	2	68	121	1.780	435
1			67	118	1.769	422
1			66	116	1.757	410
			65	113	1.744	400
1			64	111	1.730	391
			63	108	1.715	382
			62	105	1.699	374
			61	103	1.684	367
			60	100	1.670	360
1	+	3	58.6	97	1.650	350
1			50	76	1.520	290
			40	56	1.408	260
1	+	10	·	39	1.30+	240
1	+	17	i	24	1.200	224
1	+	38	10	11	1.10—	218

Pure acid of the specific gravity 1.842, is a compound of

1 atom acid . . . 5
1 atom water . . . 1·125

6.125

It is but rarely that it occurs in commerce so concentrated as this; though its specific gravity is often higher. 1.845 is a very common specific gravity of the acid of commerce, and it is frequently as low as 1.837.

<sup>\*</sup> New System of Chemical Philosophy, ii. 404.

When anhydrous sulphuric acid vapour is made to pass through a red-hot porcelain tube, it is decomposed into sulphurous acid and bxygen gases, in the proportion of two volumes of the former to one of the latter.

Freezing.

When exposed to a sufficient degree of cold, it crystallizes or freezes; and after this has once taken place, it freezes again by the application of a much inferior cold.\* Morveau froze it at — 4°; it assumed the appearance of frozen snow. After the process began, it went on in a cold not nearly so intense. The acid melted slowly at 27.5°; but it froze again at the same temperature, and took five days to melt in the temperature of 43°.+ Chaptal, who manufactured this acid once observed a large glass vessel full of it crystallized at the temperature of 48°. These crystals were in groups, and consisted of flat hexahedral prisms, terminated by a six-sided pyramid. They felt hotter than the surrounding bodies, and melted on being handled. † Chaptal has observed, that sulphuric acid, in order to crystallize, must not be too concentrated. This observation has been extended a good deal farther by Mr. Kier. He found that sulphuric acid, of the specific gravity of 1.780, froze at 45°; but if it was either much more or much less concentrated, it required a much greater cold for congelation. When as concentrated as possible, I find that it may be cooled down in thermometer tubes to the temperature of - 36° before it congeals ||.

Attracts water. Sulphuric acid has a very strong attraction for water. Neuman found, that when exposed to the atmosphere it attracted 6.25 times its own weight. Mr. Gould found, that 180 grains of acid, when exposed to the atmosphere, attracted 68 grains of water the first day, 58 the second, 39 the third, 23 the fourth, 18 the fifth, and at last only 5, 4, 3, 4, 3, &c. The 28th day the augmentation was only half a grain. The affinity, therefore, between sulphuric acid and water, as is the case in general with other substances, becomes weaker the nearer it approaches to saturation.

Action on other bodies.

Concentrated sulphuric acid has the property of dissolving several simple bodies without altering their nature. Vogel showed that the fuming acid dissolves sulphur, Muller of Reich-

† Encycl. Method. Chim. i. 376. 

‡ Jour. de Phys. xxxi. 473.

§ Phil. Trans. lxxvii. Part. ii.

See vol. i. p. 50, for the law of its congelation.

¶ Phil. Trans. 1684.

<sup>\*</sup> The freezing point was ascertained by the Duc d'Ayen in 1776. See Macquer's Dictionary.

enstein that it dissolves tellurium. Bussy found it to dissolve iodine, and it is capable also of dissolving selenium.\*

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Many of the simple bodies have the property of decomposing this acid, especially if assisted by heat. When the vapour of anhydrous acid and hydrogen gas are passed through a redhot porcelain tube, the acid undergoes decomposition and water is formed. When the vapour of the acid is passed through redhot charcoal, a similar decomposition takes place. When phosphorus is placed in contact with anhydrous sulphuric acid it takes fire and burns at the expense of the acid. Anhydrous phosphoric acid and sulphur are deposited on the inside of the tube in which the mixture was made.

When zinc or iron is thrown into sulphuric acid, a violent action takes place, if the acid be diluted; water is decomposed, its hydrogen flies off, and its oxygen combines with the metals. If the acid be concentrated, the action is much less violent, or there is none, unless heat be applied, when sulphurous acid exhales. Upon tin and copper the acid acts very slowly and feebly, unless its action be assisted by heat, when it oxidizes and dissolves them. On silver, mercury, antimony, bismuth, arsenic, and tellurium, it does not act except at a pretty high temperature. These metals abstract part of its oxygen, and convert one portion of it to sulphurous acid, while another portion combines with the oxides thus formed. When boiling hot it oxidizes lead, and dissolves cobalt, nickel, and molybdenum: but it has no perceptible action on gold nor platinum at any temperature to which it can be raised.

When assisted by heat it dissolves and destroys almost all the compound combustible bodies; though with some it has the property of uniting and forming new acids; which will be described afterwards when I come to give an account of the oxygen acids with compound bases.

It absorbs olefiant gas to the amount of two or three times its volume of it; but whether the nature of the gas is altered by this absorption, has not been ascertained.

It was accidentally discovered by Kirchhoff, a Russian che-Forms sugar, mist, that when starch is boiled for some time in dilute sulphuric acid, it is converted into sugar. Braconnot afterwards found that wood, bark, straw, hemp, and many other bodies when treated in the same way, are also converted into sugar. And he has shown more lately that when jelly or glue is dissolved in

<sup>\*</sup> Ann. de Chim. et de Phys. xxxvii. 189.

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strong sulphuric acid, and the solution boiled after sufficient dilution with water, it is converted into another species of sugar, distinguished by the great readiness with which it crystallizes.\*

Many vegetable substances containing charcoal as a constituent, blacken sulphuric acid. The reason seems to be, that in consequence of the great affinity of this acid for water, the oxygen and hydrogen of the body unite and form water, and thus the charcoal being disengaged blackens the acid. If we dilute the acid with water the charcoal falls in the state of a black powder. If we boil the acid the charcoal is acidified at the expense of the acid, which in consequence becomes again limpid and colourless.

I have already shown (Vol. I. p. 263), that sulphuric acid is a compound of

1 atom sulphur	•	•	<b>2</b>
3 atoms oxygen	•	•	3
			5

Anhydrous acid how formed,

Berzelius assures us that anhydrous sulphuric acid may be procured by the following process: Mix three parts of anhydrous sulphate of soda with two parts of concentrated sulphuric acid of commerce, and gradually heat the mixture in a covered crucible to incipient redness, till the boiling occasioned by the escape of the water of the acid has ceased. When the mass formed has cooled, break it in pieces and put it into a porcelain retort, and distil at a red heat. The acid which comes over is to be collected in a glass receiver surrounded with ice. acid becomes solid in the receiver. It has usually a dark colour, and is not absolutely free from water. Hence it forms crystals destitute of the tenacity, and quite different in their appearance from perfectly anhydrous acid. But if we distil it again at a low temperature, we will obtain perfectly anhydrous acid.+

Doubtless the sesquisulphate of soda, which is anhydrous and easily obtained, might be employed with advantage for furnishing anhydrous sulphuric acid.

There are few acids more powerful than sulphuric acid. On this account, and also on account of its cheapness, it is more employed in chemical processes than any other acid whatever.

<sup>\*</sup> Ann. de Chim. et de Phys. xiii. 113. † Berzelius, Chimée, ii. 8.

## 2. Sulphurous Acid.

Sulphurous acid is usually prepared by heating a mixture of Formation. sulphuric acid and mercury in a small retort. The gas must be collected over mercury. When our object is to prepare it in large quantity, as for the formation of sulphites, a good method is to mix sulphuric acid with the sawings of wood, and apply heat to the mixture in a retort. Berthier recommends a mixture of four parts of flowers of sulphur, with five parts of teroxide of manganese reduced to fine powder. He says that half the sulphur is converted into sulphurous acid, while the other half unites with the protoxide of manganese. I tried this process, but no sulphurous acid was extricated by the heat of a spirit lamp.

Sulphurous acid at the usual temperature of the atmosphere Liquefaction.

is a gas. But Mr. Faraday discovered that by a pressure of two atmospheres this gas might be condensed into a liquid at the temperature of 45°. M. Bussy has since examined the liquefaction of this gas, and shown that it may be produced by means of a freezing mixture. He first passed the gas through a vessel surrounded with ice, to condense the greatest part of the aqueous vapour which it contained, and to dry it completely; it then passed through a tube filled with fragments of dry chloride of calcium. It finally passed into a small matrass, surrounded by a freezing mixture composed of two parts of snow or ice and one part of common salt. In this last vessel the gas condenses under the mere pressure of the atmosphere.

Liquid sulphurous acid is a transparent colourless liquid, of the specific gravity 1.45.\* It boils at the temperature of 14°, but produces so much cold by evaporating, that a portion of it continues for some time liquid even in the open air. If a little of this liquid be dropt upon water in a watch glass, the cold produced by its evaporation speedily converts the water into ice. Even mercury may be frozen in the same way, by covering a globule of it with this liquid acid and placing it in the vacuum of a receiver.† By this process M. Bussy sunk a thermometer to — 66°.

M. de la Rive found that liquid sulphurous acid is a non-conductor of electricity, but it becomes a conductor when a little water is added to it. Its refracting power, according to his

<sup>\*</sup> Faraday states it at 1.42, which differs but little.

<sup>†</sup> Ann. de Chim. et de Phys. xxvi. 63.

experiments, differs very little from that of water, and is certainly not less than the refracting power of that liquid. M. de la Rive discovered that when liquid sulphurous acid is prepared by Bussy's method, white crystals are formed in the first tube surrounded by ice. These crystals are white, have a sour taste, and are in the state of thin plates similar to the solid decihydrate of chlorine. They remain solid at the temperature of about 40°. But at that temperature they begin to give out gas, and when the temperature is a little more elevated they are entirely resolved into sulphurous acid gas and water.\* According to de la Rive's experiments, these crystals are composed of

2 sulphurous acid, 8 water.

This approaches nearly to

But he is of opinion that the quantity of acid was greater than what he obtained, and is inclined to consider the crystals as composed of

I atom sulphure	•	•	4		
10 atoms water	•	. •	•	•	11.25
					15.25

Absorption by water.

Water, by my trials, absorbs 33 times its volume of sulphurous acid gas. But Saussure obtained an absorption amounting to  $43\frac{3}{4}$  volumes, while alcohol absorbed  $115\frac{3}{4}$  volumes. The specific gravity of the saturated solution I found 1.0513. The water saturated in my trials was a compound of about 39 atoms water and 1 atom acid. Saussure (who probably made his experiments at a lower temperature than I did) obtained an acid rather stronger, but still very weak.

This water may be frozen without parting with any of the acid gas. When water, which has been saturated with this acid at the freezing temperature, is exposed to the heat of 65.25°, it is filled with a vast number of bubbles, which continually increase and rise to the surface. These bubbles are a part of the acid separating from it. It freezes a few degrees below 32°.+

<sup>\*</sup>Ann. de Chim. et de Phys. xl. 401.

<sup>†</sup> Fourcroy and Vauquelin, Nicholson's Jour. i. 513.

Oxygen gas and sulphurous acid gas do not combine at the common temperature of the air if they are kept dry. water be present they gradually combine, and are converted into sulphuric acid. When passed through a red-hot tube, or when electrical sparks are passed through the mixture, they combine likewise and constitute sulphuric acid.

Sulphurous acid is one of the weakest of the acids. salts which it forms with bases have received the name of sul-When exposed to the air in solution in water, they gradually absorb oxygen and are converted into sulphates.

It is readily decomposed by potassium and sodium. dissolves iron without the evolution of any gas, as was first observed by Mr. Higgins.\* When exposed to the action of peroxide of lead it is absorbed, as Berzelius first ascertained, and the peroxide converted into common sulphate of lead.+ Peroxide of manganese produces a similar change in this acid. The action of the remaining metals and their oxides on this acid gas is still imperfectly known.

This acid does not redden vegetable blues but destroys them, Action on vegetable colprovided it be free from all admixture of sulphuric acid. the petals of a red rose be put into sulphurous acid, they immediately become white, but recover their red colour again if plunged into diluted sulphuric acid. In consequence of this property which it has of destroying colours, the fumes of burning sulphur are employed for bleaching flannel.

Sulphuric acid absorbs this gas in considerable quantities. It is absorbed also by borax, as was first observed by Dr. Priestley, and may by its means be separated from carbonic acid when they happen to be mixed together. Mr. Accum says that it is decomposed over mercury, and sulphur deposited, if it be brought in contact with protochloride of tin.

I have already shown (Vol. I. p. 263) that this acid is a compound of

> l atom sulphur 2 atoms oxygen 4

so that its atomic weight is 4.

## 3. Subsulphurous Acid.

It was first observed by Vauquelin that zinc dissolves in Discovery. sulphurous acid without the evolution of any gas, and that the

<sup>\*</sup> Higgins' Comparative View, p. 49. † Phil. Trans. 1813, p. 186.

solution when evaporated yields a peculiar salt, which he distinguished by the name of sulphuretted sulphate of zinc. the solution be conducted by a uniform and not too copious stream of sulphurous acid gas, there is no effervescence what-But when the supply of acid is too great, the liquid becomes hot, and an effervescence takes place. When the solution has made a certain progress it has at first a brownish yellow colour, but this colour disappears as the process goes on. When this solution is evaporated it becomes a thick white magma, in which crystals consisting of four-sided prisms make their appearance. The salt thus obtained is in general a mixture of sulphite and subsulphite of zinc, but we may separate them by means of alcohol, which leaves the sulphite, but dissolves the subsulphite of zinc. This last salt dissolves both in water and alcohol. It has a pungent and excessively disagreeable taste. If we drop an acid into its aqueous solution an effervescence takes place, and abundance of sulphur precipitates.

I consider this salt as a compound of oxide of zinc and a peculiar acid of sulphur, to which, for want of a better name, I have given the appellation of subsulphurous acid. I have made some attempts to procure this acid in a separate state, but they were unsuccessful. It seems to undergo decomposition the instant it is separated from the oxide of zinc. There is no difficulty, however, in determining the proportion of its consti-Sulphurous acid is a compound of

> 1 atom sulphur 2 atoms oxygen.

When it is made to act upon zinc, it dissolves the metal without effervescence. But the zinc is converted into an oxide in the first place, and for this change every atom of it requires to combine with an atom of oxygen. This oxygen is supplied by the sulphurous acid. And as every atom of the acid is capable of combining with an atom of oxide of zinc, it is clear that the acid must part with half of its oxygen to oxidize the zinc. composition. Consequently the subsulphurous acid which exists in the salt must be a compound of

1 atom sulphur 1 atom oxygen 3

and its atomic weight must be 3.

When an acid separates this acid from the oxide of zinc, it resolves itself into sulphurous acid and sulphur. One half the

sulphur precipitates, and acid thus altered is obviously reduced to the state of common sulphurous acid.

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When sulphurous acid is made to act upon iron, a subsulphite of iron is formed quite similar to the subsulphite of zinc, but it is not known whether any of the other metals are capable of inducing a similar change.

It is affirmed, that if sulphite of zinc be boiled in a close vessel with sulphur it is converted into neutral subsulphite of zinc. I have not tried this experiment, but if it be correct, it would indicate that subsulphurous acid is a compound of

2 atoms sulphur	•	•	4
2 atoms oxygen	•	•	2
			-
			6

and that its atomic weight was 6. But this explanation would not accord with the known fact that zinc is oxidized by sulphurous acid without effervescence. The salt formed by boiling sulphite of zinc and sulphur ought to be a bisubsulphite of zinc.

### 4. Hyposulphurous Acid.

For our knowledge of the existence of this acid we are indebted to Mr. Herschell. He formed a numerous class of salts to which he gave the name of hyposulphites.\*

When sulphuret of calcium is dissolved in water we obtain a greenish yellow coloured solution having the smell of sulphuretted hydrogen gas, and precipitating all the metals from their solutions. If this liquid be preserved for some time, it gradually becomes colourless and loses its peculiar smell. If it be now evaporated it yields large crystals, most commonly in the state of six-sided prisms, and having an exceedingly bitter taste. They consist of hyposulphurous acid and lime united together in the following proportion, according to Mr. Herschell's analysis:

Hyposu	ılphu	rous a	acid		•	36.64
Lime	•	•	• .•	•		22.14
Water	•	•	:	•	•	41.22
						100.00

From this salt, which is easily procured by passing a current of sulphurous acid gas through hydroguretted sulphuret of lime, the other hyposulphites may be readily obtained. These salts are colourless, and, with an exception or two, they are soluble in water. Their taste is most commonly bitter; though some of the metalline hyposulphites have an intensely sweet taste.

I have stated (Vol. I. p. 267) that an examination of a hydrosulphuret of soda which accidentally crystallized in Mr. Tennant's soda leys during the warm summer of 1825, and the conversion of it into hyposulphite of soda by means of sulphurous acid, left no doubt that this acid is a compound of

0 -4	(		A
2 atoms sulphur	•	•	4
1 atom oxygen	•	•	Į l
			5

and this was confirmed by the direct analysis of some of Mr. Herschell's hyposulphites formed by the process which he gives in his paper. Gay-Lussac is of opinion that hydrogen also enters into the composition of this acid.\* But if this were so, it would be impossible to account for the precipitation of sulphur when sulphurous acid is mixed with a solution of hydrosulphuret of soda. But hyposulphurous acid differs from the bisulphuretted hydrogen of Berthollet merely by the substitution of an atom of oxygen for the atom of hydrogen which the bisulphuretted hydrogen contains.

Hyposulphurous acid cannot exist in a separate state. When we attempt to decompose the hyposulphites, we always resolve their acid into sulphurous acid and sulphur.

# 5. Hyposulphuric Acid.

I have already stated the history of the discovery of this acid, the method of obtaining it, and the properties which it possesses, in the first volume of this work (p. 269).

It dissolves zinc with the disengagement of hydrogen gas. When cold it is not altered by chlorine, concentrated nitric acid, or red sulphate of manganese. It saturates the different bases, and seems to form soluble salts with all of them. To these salts the name of hyposulphates has been given.

Gay-Lussac and Welter have shown that this acid is a compound of 1 integrant particle of sulphuric acid and 1 integrant particle of sulphurous acid united together. Hence its constituents must be

<sup>\*</sup> Ann. de Chim. et de Phys. xiv. 361.

2 atoms sulphur = 45 atoms oxygen = 5 Class I. Div. I.

9

and the equivalent number for it must be 9.

The salts which this acid forms (and which are very curious) have been examined in detail by Dr. Heeren of Hamburg.† An account of them will be given in a subsequent part of this work.

#### SECTION VIII.—ACIDS OF SELENIUM AND TELLURIUM.

Selenium, so far as we know at present, forms only two acids with oxygen, analogous, so far as their composition goes, to the sulphurous and sulphuric acids. These acids are the selenious and selenic acids.

#### 1. Selenic Acid.

I have given the history, preparation, and properties of this acid so far as they are known in the first volume of this work (p. 290). It is a compound of

1 atom selenium . . . 5
3 atoms oxygen . . . 3

Of consequence it is similar to sulphuric acid in its composition. The salts of this acid called *seleniates*, have hitherto been very imperfectly examined. They almost exactly resemble the corresponding sulphates. But we may distinguish them by the property which they have of detonating when heated to redness with charcoal, and by disengaging chlorine when boiled with muriatic acid. The acid is disengaged from its bases by sulphuric acid. Selenic and sulphuric acid are isomorphous bodies.

### 2. Selenious Acid.

This is the acid to which Berzelius in his original paper on selenium gave the name of selenic acid. I have described the method of obtaining it and some of its properties in the first volume of this work (p. 290):

When the crystals of this acid are exposed to the air, they lose their lustre and adhere to each other, doubtless by absorbing moisture from the atmosphere, but they do not deliquesce.

<sup>\*</sup> See Annals of Philosophy, xiv. 352.

<sup>+</sup> Poggendorf's Annalen, vii. 70 and 171.

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The taste of the acid is sour and hot, and its smell when in the state of vapour is similar. It is exceedingly soluble in boiling water, and crystallizes as the saturated solution cools. It dissolves also abundantly in alcohol, and when the solution is heated it gives out the smell of ether. But Berzelius did not succeed in obtaining any other by distilling a solution of alcohol saturated with this acid. A plate of zinc or of iron put into a solution of selenious acid in water, throws down selenium. And according to Fischer, selenium is thrown from it by all the metals which precipitate silver from its solution in nitric acid. But selenium is not precipitated by any of these metals from selenic acid, showing that this last is more difficult of decomposition than the selenious acid.

The selenium is easily precipitated from this acid, and also from the selenites (as the salts which it forms are called), by adding an acid to the solution, and then mixing it with sulphite of ammonia. The selenium precipitates in about 12 hours, but not completely unless we boil the liquid for some time, adding occasionally sulphite of ammonia. The constituents of this acid are

1 atom sclenium	•	•	5
2 atoms oxygen	•	•	<b>2</b>
			7

It is a pretty powerful acid, though less so than selenic acid. It decomposes nitrate of silver and nitrate of lead. And when assisted by heat, it disengages both nitric and muriatic acid from fixed bases. But as it is itself volatile, it is displaced in its turn by sulphuric, phosphoric, arsenic, and boracic acids.

### 3. Telluric Acid.

The oxide of tellurium possesses both the properties of an acid and a base. I have already given an account of its characters, so far as they have been determined, in the first volume of this work.

# SECTION IX.—REMAINING OXYGEN ACIDS WITH A SIMPLE BASE.

It is unnecessary to enter into any farther details respecting the remaining 12 oxygen acids with simple bases, as all their properties, so far as I am acquainted with them, have been already given under the respective metals which constitute their bases. I shall merely state their names to recall them to the recollection of the reader. 1. Arsenic forms two acids, the arsenious and arsenic, the last of which Mitcherlich has shown to be isomorphous with the phosphoric acid.

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- 2. Antimony forms two acids, the antimonious and antimonic, similar in their constitution to the arsenious and arsenic. Rose has shewn that arsenic and antimony are isomorphous bodies. The acids of the two metals being similarly constituted, ought also to be isomorphous bodies.
- 3. Chromium forms only one acid similar in its constitution to the phosphoric, arsenic, and antimonic. Whether it be isomorphous with them has not hitherto been examined.
- 4. The peroxide of uranium possesses the double property of combining with bases and with acids. Hence it might be called *uranic acid*.
- 5. The molybdic, tungstic, columbic, and titanic acids, require no additional remarks to those made while treating of them respectively in the first volume of this work.
- 6. The oxide which I described in the first volume of this work (p. 516), under the name of bin-oxide of manganese, seems, as I have mentioned before, to be capable of combining in definite proportions with bases. Thus the species of manganese ore, to which Haidinger has given the name of Psilomelanite, appears from the analysis of Dr. Turner to be a compound of

3 atoms subsesquihydrate of binoxide,

1 atom quadromanganite of barytes.

By quadromanganite of barytes, I mean a compound of 4 atoms binoxide of manganese with one atom of barytes. I have also formed definite compounds of this oxide and lime. From this there seems little doubt that it possesses acid properties. It might therefore be called *manganous acid*.

Manganic acid possesses decided acid characters.

It is curious to see an alkalifiable base like manganese assuming acid properties, when it combines with more oxygen than exists in the alkaline compounds of the same base and oxygen. Tin and gold seem to possess similar characters, and probably the remark might be applied to the greater number of the bodies which have been placed under the division of noble bases.

# DIVISION II.-ACIDS WITH A COMPOUND BASE.

The acids of oxygen, with a compound base, are very numerous, and are daily augmenting as chemists extend their

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researches into the animal and vegetable kingdoms of nature. The double base consists most commonly of carbon and hydrogen; sometimes of carbon, hydrogen, and azote; and there are a few of them into which sulphur enters likewise as a constituent. Doubtless the number of constituents which enter into these compound bases, will increase very much hereafter, when the nature of these compound acids has been more completely investigated.

Many of these acids exist ready formed in the vegetable kingdom, and require only to be disengaged from the other vegetable substances with which they are mixed or combined in the part of the plant which contains them. This is the case with tartaric acid, which exists ready formed in grapes, with malic acid which exists in apples, and with citric acid which gives acidity to lemons and limes. Some are formed by a species of fermentation, to which certain vegetable substances Thus acetic acid is formed by the fermentation of are liable. various species of sugar. There are others which are formed during the distillation of certain vegetable bodies. Thus pyrotartaric acid is formed during the distillation of tartaric acid, and pyrocitric acid during the distillation of citric acid. Nitric acid has the property of converting various vegetable and even animal substances into acids. In this way mucic acid, camphoric acid, suberic, and various other acids, are formed. And finally, there are other acids, formed by the combination of sulphuric acid with certain vegetable substances.

The following table contains the names of all the oxygen acids with compound bases that have been hitherto examined. Our present knowledge of their constitution is too limited to enable us to adopt a systematic arrangement. But in the following table they are divided into sets according either to the number or nature of the compound bases which are combined with the oxygen.

Table of compound acids.

## A. Acids composed of Oxygen united to Carbon and Hydrogen.

1. Acetic,	10. Pyromalic,	19. Kinic,
2. Formic,	11. Mucic,	20. Pyrokinic,
3. Mellitic?	12. Pyromucic,	21. Meconic,
4. Tartaric,	13. Succinic,	22. Boletic,
5. Vinic,	14. Benzoic,	23. Camphoric,
6. Pyrotartaric,	15. Croconic?	24. Suberic,
7. Citric,	16. Gallic,	25. Pectic.
8. Pyrocitric,	17. Ulmic,	
9. Malic,	18. Crameric,	

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# B. Fatty Acids composed of the same Ingredients.

I. Solid. 1. Stearic. 2. Margaric, 3. Capric, 4. Ricinic,

5. Cevactic, II. Liquid.

6. Oleic,

7. Phocenic,

8. Butyric,

9. Caproic,

10. Hircic. 11. Elaiodic,

12. Crotonic,

III. Not Soapifiable.

13. Ambreic.

14. Cholesteric.

- C. Resinous Acids composed of the same Constituents.
- 1. Pinic.
- 2. Colophonic,
- 3. Silvic.
- D. Acids composed of Oxygen, Carbon, and Azote.
- 1. Carbazotic,
- 2. Indigotic,
- 3. Uric.
- E. Acids composed of Oxygen, Hydrogen, Carbon, and Azote.
  - 1. Aspartic,
- 3. Nitroleucic, 5. Purpuric,
- 2. Nitrosaccharic, 4. Pyruric,
- 6. Allantoic.
- F. Acids composed of Oxygen, Hydrogen, Carbon, and Sulphur.
  - 1. Hydro-carbosulphuric, 4. Sulphonapthalic,

2. Sulphovinic,

5. Vegetosulphuric.

- 3. Xanthic.
- G. Acids composed of Oxygen, Hydrogen, Carbon, Azote, and Sulphur.

## 1. Sinapic.

The peculiar nature of the whole of these acids has not yet been made out in a satisfactory manner. But it is proper to notice them all in a work of this kind, in order to draw to them the attention of practical chemists, that all uncertainty respecting them may be removed as speedily as possible. shall describe them in the following sections.

#### SECTION I .-- OF ACETIC ACID.

This acid is employed in three different states, which have states. been distinguished from each other by peculiar names. When first prepared, it is called vinegar; when purified by distillation, it assumes the name of distilled vinegar, usually called acetous

acid by chemists; when concentrated as much as possible by peculiar processes, it is called radical vinegar, and by chemists acetic acid. It will be requisite to describe each of these states separately.

History.

1. Vinegar was known many ages before the discovery of any other acid, those only excepted which exist ready formed in vegetables. It is mentioned by Moses, and indeed seems to have been in common use among the Israelites and other eastern nations at a very early period. It is prepared from wine, from beer, ale, and other similar liquids. These are apt, as every one knows, to turn sour, unless they be kept very well corked. Now sour wine or beer is precisely the same with vinegar.

Boerhaave describes the following method of making vinegar, which is said to be still practised in different places:

Formation.

Take two large oaken vats or hogsheads, and in each of these place a wooden grate or hurdle at the distance of a foot from the bottom. Set the vessel upright, and on the grate place a moderately close layer of green twigs of fresh cuttings of the vine. Then fill up the vessel with the footstalks of grapes, commonly called the *rape*, to the top of the vessel, which must be left quite open.

Having thus prepared the two vessels, pour into them the wine to be converted into vinegar, so as to fill one of them quite up, and the other but half full. Leave them thus for twenty-four hours, and then fill up the half-filled vessel with liquor from that which is quite full. Four-and-twenty hours afterwards repeat the same operation; and thus go on, keeping the vessels alternately full and half full during every twenty-four hours till the vinegar be made. On the second or third day there will arise, in the half-filled vessel, a fermentative motion, accompanied with a sensible heat, which will gradually increase from day to day. On the contrary, the fermenting motion is almost imperceptible in the full vessel; and as the two vessels are alternately full and half full, the fermentation is by that means, in some measure, interrupted, and is only renewed every other day in each vessel.

When this motion appears to have entirely ceased, even in the half-filled vessel, it is a sign that the fermentation is finished; and therefore the vinegar is then to be put into casks close stopped, and kept in a cool place. The process in summer usually lasts fifteen days; in winter it lasts longer.\*

\* An account of the mode of making vinegar in France, almost precisely the same with that given in the text, was published in the Philosophical

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Vinegar in this country is usually made not from wine but from the malt of barley. This malt is ground and mashed with hot water. The sweet solution, known by the name of wort, is drawn off and fermented in the usual way. It is then put into barrels, which are arranged in stores with their bungs out, and kept in a temperature of about 84°. The liquid is gradually changed into vinegar.

Of late years a great deal of vinegar is made in this country wood vinegar. by the distillation of wood (chiefly the branches of trees). The matter which comes over consists of a mixture of pyroligneous spirit, acetic acid, empyreumatic oil, &c. The liquid products are separated from the solid, and being saturated with lime the whole is subjected to distillation. The first product obtained is the pyroligneous spirit. The pyrolignate or acetate of lime formed is decomposed by sulphate of soda by double decomposition, acetate of soda and sulphate of lime being formed. The liquid containing the acetate of soda is evaporated to dryness, and the dry residue exposed to a heat of about 550°, which chars the impurities mixed with the salt. It is then dissolved in water, filtered, evaporated to dryness, and mixed with the requisite quantity of sulphuric acid to saturate the soda. The mixture being subjected to distillation, the acetic acid comes over pure, and its strength depends upon the quantity of water which the salt contained when mixed with the sulphuric acid.

Vinegar is a liquid of a reddish or yellowish colour, a pleasant Properties of vinegar. sour taste, and an agreeable odour. Its specific gravity varies from 1.0135 to 1.0251, and it differs also in its other properties according to the liquid from which it has been procured. It is very subject to decomposition; but Scheele discovered, that if it be made to boil for a few moments, it may be kept afterwards for a long time without alteration. Besides acetic acid and water, vinegar contains several other ingredients, such as mucilage, a colouring matter, and often also two or more vegetable acids. When distilled at a temperature not exceeding that of boiling water, till about two-thirds, or five-sixths at most. of it have passed over, most of these impurities are left behind. and the product is pure acid, diluted with water. The residuum is still an acid liquid, and often lets fall crystals of tartar. But

Transactions for 1670, vol. v. p. 2002. The methods at present practised in France are described in the 3d volume of the Elemens de Chymie, published by the Dijon Academy, p. 6. Many still follow the process described in the text; others a different one.

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even when thus distilled it is not quite pure. Mr. Chenevix has shown that it still contains a peculiar mucilaginous or extractive matter, and traces of a spirituous liquor.

Mr. Phillips informs us that when the best English malt vinegar of the specific gravity 1.0204 is distilled, the first eighth is of the specific gravity 0.99712,\* and a fluid ounce of it (1.8047 cubic inches) dissolves from 4.5 to 5 grains of precipitated carbonate of lime. The next six-eighths have the specific gravity 1.0023, and a fluid ounce dissolves 8.12 grains of precipitated carbonate of lime. A fluid ounce of acid of the specific gravity 1.007 dissolves from 15 to 16 grains of precipitated carbonate of lime, or 13.8 grains of marble.

Distilled vinegar. 2. The acid thus obtained is a liquid as transparent and colourless as water, of a strong acid taste and an agreeable odour, somewhat different from that of vinegar. In this state it is usually called acetous acid or distilled vinegar.

It may be preserved without alteration in close vessels.

When exposed to a moderate heat, it evaporates completely, and without undergoing any change in its properties. When exposed to the action of cold part of it congeals. The frozen portion, which consists almost entirely of water, may be easily separated; and by this method the acid may be obtained in a high degree of concentration. The more concentrated the acid is, the greater is the cold necessary to produce congelation. Mr. Lowitz has ascertained that the acid itself how much soever it be concentrated, crystallizes or congeals at the temperature of — 22°.

R**a**dical vinegar. 3. Radical vinegar or acetic acid, as it is now called, was originally obtained by distilling verdigris or acetate of copper in a retort, and then rectifying the liquid that comes over by a second distillation. This process was known to the alchymists; and the liquid obtained was distinguished by the name of radical vinegar. Berthollet, in 1785, endeavoured to show that it differed essentially from distilled vinegar or acetous acid (as it was then called), and he was of opinion that it contained a greater quantity of oxygen. M. Adet in 1797 published a set of experiments, from which he concluded that there was no other difference except concentration between acetous and acetic acid or radical vinegar.

<sup>\*</sup> It must have contained a portion of alcohol mixed with it, for the sp. gr. of acetic acid is greater than that of water.

<sup>†</sup> Phillips on the Pharmacopæia Londinensis, p. 7.

<sup>†</sup> Ann. de Chim, xxvii. 299.

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This conclusion was considered as hasty, as he did not attempt to account for the very striking difference in the taste and smell of these acids, as he had neither repeated nor refuted the experiments of Berthollet, on which the opinion of the difference between these two acids was founded. The conclusion of Adet was opposed, in 1798, by Chaptal, who published a set of experiments on the same subject.\* This philosopher endeavoured to demonstrate, as Berthollet had done before him, that acetic and acetous acids, even when of the same strength, possess different properties, and have different effects on other bodies. From the effect of sulphuric acid upon each, and from the quantity of charcoal which remains in the retort when equal quantities of each saturated with potash are distilled, he concluded that acetous acid contains a smaller proportion of carbon than And this he considered as the cause of the differacetic acid. ence in their properties.

In 1800, a new set of experiments on the same subject was published by Mr. Dabit of Nantes.† This chemist endeavoured to prove that acetic acid contains a greater proportion of oxygen than acetous. When he distilled a mixture of acetate of potash and sulphuric acid, the product was acetic acid; but when he substituted muriatic acid for sulphuric, he obtained acetous acid: but when to this last mixture a little black oxide of manganese was added, he assures us that he obtained acetic acid. And in none of these cases was there any carbonic acid emitted till towards the end of the distillation.

The experiments of Darracq at last finally settled this dispute by demonstrating that acetous and acetic acids differ merely in concentration. This able chemist repeated the experiments of Adet, which he found perfectly accurate, and performed several new ones; all of which left no doubt that acetous and acetic acids contain precisely the same proportion of oxygen. next tried the opinion of Chaptal respecting the proportion of carbon in each. When equal quantities of acetic and acetous acids are combined with potash or soda, the dry salts distilled leave the same quantity of charcoal, and yield the same quantity of other products. When reduced to the same specific gravity, the two acids form precisely the same salts with all alkaline and earthy bases. Finally, acetous acid gradually becomes acetic acid when distilled repeatedly off dry muriate of lime; and in this case no gaseous body whatever is evolved.

From these facts, it is impossible to entertain a doubt that the two substances are essentially the same, and that these apparent differences are owing to the great quantity of water with which acetous acid is diluted, and the mucilaginous matter which it still retains.\* The same results were obtained also by Proust, who had drawn the same conclusions before he became acquainted with Darracq's paper.† In consequence of these facts, the term acetous acid has been laid aside, and the name acetic acid is now given by chemists to pure vinegar in all its states of concentration.

Acetic acid in its greatest degree of concentration may be obtained by mixing anhydrous acetate of lead, or acetate of soda, with the quantity of concentrated sulphuric acid requisite to saturate the bases of these salts, and distilling with a gentle heat. The liquid that comes over is not quite free from sulphurous acid. The addition of a little peroxide of lead throws down the sulphurous acid by instantly converting it into sulphuric acid. To be sure that it contains no oxide of lead in solution, it is necessary to subject the acid to a new distillation.

Characters of acetic acid.

Acetic acid obtained by this process is a compound of one atom of acetic acid and one atom of water. It crystallizes at the temperature of 45° when we throw into it any particle of solid matter (a crystal of acetic acid answers best), and the thermometer plunged into it rises at the same time from 45° These crystals are usually flat plates, and they have a pearly lustre. The smell of the acid in this state is so strong as to be painful to the olfactory organs. Its taste is excessively sour, and when applied to the skin it blisters the place and pro-These crystals melt into a liquid at a temperaduces a sore. ture rather below 60°, though I have not been able to determine the exact point. The specific gravity of the liquid crystals The following table exhibits the specific at 60°, is 1.06296. gravity of these crystals in solution, and combined with various quantities of water.

Acid.		Water.			Sp. gravity at 60°.
1 atom	+	l atom	4	•	1.06296
1	+	<b>2</b>	•	•	1.07060
1	+	3	٠.	•	1.07084
1	+	4	•	•	1.07132
1	+	5	•		1.06820
1	+	6	•	•	1.06708

<sup>\*</sup> Darracq, Ann. de Chim. xli. 264.

Acid.		Water.			Sp. gravity at 60°.
1 atom	+	7 atoms	•	•	1.06349
1	+	8	•		<b>1</b> ·05974
1	+	9	•	•	1.05794
1	+	10	•	•	1.05439

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From this table it appears that the specific gravity is a maximum, when the liquid is a compound of 1 atom acid and 4 atoms water, or of 100 parts acid and 72 parts water. We see also that the specific gravity of acid containing only one atom water is nearly the same with that containing 7 atoms water.\* It is evident from this that no information respecting the strength of the acid can be obtained from its specific gravity.

Acetic acid possesses but little energy in combining with bases; as most of the other acids are capable of displacing it. But it neutralizes most bases very well, and forms with them a class of salts called acetates, several of which are of considerable importance. They are all without exception soluble in water. The least soluble are the acetates of mercury and silver, but they are not sufficiently so to enable us to employ them as means of determining the quantity of acetic acid in any compound.

Acetic acid requires a strong red heat for its decomposition. Mr. Chenevix passed it five times successively through a red hot porcelain tube without destroying it completely. But when the tube is filled with charcoal, the decomposition is complete.

The first attempt to ascertain the constituents of acetic acid Composition. was made by Dr. Higgins. He distilled acetate of potash, and by that means decomposed the acetic acid. The products were collected and examined.+ But at that time chemistry was not far enough advanced to entitle us to look for correct results from The subject was resumed, first by Gaysuch an analysis. Lussac and Thenard, and afterwards by Berzelius. The former burnt a mixture of acetate of barytes and chlorate of potash. The acid was completely converted into water and carbonic acid. The gaseous products being examined, and the quantity of acetic acid decomposed known, they were enabled to calculate its constituents.‡ Berzelius' analysis was conducted according to the same theoretical principles. But he was at more pains to obtain the salt upon which he operated quite free from water.§

First Principles, ii. 138. † Higgins on Acetous Acid, p. 26. \*

<sup>‡</sup> Recherches Physico-chymiques, ii. 308.

<sup>§</sup> See a minute account of the precautions which he took, and the mode which he followed, in the Annals of Philosophy, iv. 323.

The following table exhibits the composition of acetic acid according to these chemists:

	_	Hydrogen.		Carbon,		Oxygen.		
Gay-Lussac		5.629	+	50.224	+	44.147	=	100 acid
								100 acid

But Berzelius has corrected these first results, and now considers the constituents of acetic acid to be.

Oxygen	•			46.642
-Carbon	•	•		47.536
Hydrogen	•	•	•	5.822

100.000

Now these numbers are meant to be the equivalents for

3 atoms oxygen	•	•	3.0
4 atoms carbon	•	•	3.0
3 atoms hydrogen	•	•	0.375
			6:375

Atomic weight.

This would make the atomic weight 6.375. I have given an account elsewhere of a careful set of experiments which I made to determine the atomic weight of acetic acid.\* I obtained as the result 6.25. This differs from the analysis of Berzelius by an atom of hydrogen—a quantity so small that it is not easy to devise experiments of a nature capable of deciding the point with absolute certainty. But my experiments being simple and easy, I am induced to put some confidence in them. I therefore consider the constituents of this acid to be

3 atoms oxygen	•	•	3
4 atoms carbon	•	•	3
2 atoms hydrogen	•	•	0.25
			6.25

Several other determinations have been published; but none of them seem to have been founded on direct experiment except those of Gay-Lussac, Berzelius, and my own.

Acetic acid is formed in great abundance during the slow combustion of alcohol, ether, and volatile oils, by means of a coil of platinum wire, by the method discovered by Sir H. Davy. Mr. Daniel considered the acid formed by this process as peculiar, and he described it under the name of *lampic* acid. I stated in the last edition of this work my opinion that it was

<sup>\*</sup> Annals of Philosophy (2d series), ii. 142, and First Principles, ii. 127.

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merely acetic acid, disguised by the presence of some foreign matter. And the accuracy of this opinion was soon afterwards established by Mr. Daniel himself. There is a curious set of experiments by Mr. Miller, showing that a great variety of substances after being heated, when brought in contact with the vapour of ether, maintain a slow combustion, and give origin to the formation of a great deal of acetic acid.\* The subject is highly worthy of a particular investigation.

There are three acids which have been distinguished by peculiar names, but which seem to be nothing else than acetic acid, a little disguised by the presence of foreign matter. It will be worth while to give a short account of these acids in this place.

#### 1. Lactic Acid.

When milk is kept for some time it turns sour; Scheele examined the acid thus evolved, and gave it the name of *lactic acid*. He directs the following method of procuring it:

Evaporate a quantity of sour whey to an eighth part, and then filter it: this separates the cheesy part. Saturate the liquid with lime-water, and the phosphate of lime precipitates. Filter again, and dilute the liquid with three times its own bulk of water; then let fall into it oxalic acid, drop by drop, to precipitate the lime which it has dissolved from the lime-water; then add a very small quantity of lime-water, to see whether too much oxalic acid has been added. If there has, oxalate of lime immediately precipitates. Evaporate the solution to the consistence of honey, pour in a sufficient quantity of alcohol, and filter again; the acid passes through dissolved in the alcohol, but the sugar of milk and every other substance remains behind. Add to the solution a small quantity of water, and distil with a small heat; the alcohol passes over and leaves behind the lactic acid dissolved in water.+

From the properties of the acid procured by this process, Scheele concluded that it was very analogous to the acetic, but that it wanted something to bring it to that state. He even pointed out a method of procuring vinegar from milk in considerable quantity, and ascertained that it always yielded a little when distilled.‡

In the year 1802, Bouillon Lagrange published a set of

<sup>\*</sup> Annals of Philosophy (2d series), xii. 17.

<sup>†</sup> Scheele, Kongl. Vet. Acad. Handl. 1780, p. 116. ‡ Scheele, ii. 66.

experiments on lactic acid, from which he drew as a conclusion that it is merely acetic acid contaminated with some saline and animal matter.\* Thenard drew the same conclusion from his experiments in 1806.† Both of these chemists had obtained the acid which they examined by distillation. But Scheele had expressly stated, that lactic acid when distilled was converted into acetic acid. The existence of lactic acid, therefore, was by no means disproved by their experiments. The subject was taken up by Professor Berzelius, in 1808. In the second volume of his Animal Chemistry, he examined the properties of lactic acid in detail, and endeavoured to establish its peculiar nature.‡ He employed the following process for procuring pure lactic acid:

Extract obtained by evaporating whey to dryness, consists of lactic acid, lactate of potash, muriate of potash, phosphate of lime, and some animal matter. It was dissolved in alcohol and mixed with alcohol, holding  $\frac{1}{76}$ th of its weight of concentrated sulphuric acid till there was an excess of sulphuric acid in the solution. Some sulphate of potash was precipitated. To get rid of the other acids it was digested over carbonate of lead, till the liquid acquired a sweetish taste. By this the sulphuric acid, the phosphoric acid, and most of the muriatic acid, were separated; but lactic acid forming a soluble compound with lead remained in solution. A current of sulphuretted hydrogen gas being passed through the liquid threw down the lead. liquid was now digested over quicklime till all the animal matter was separated. It now contained only lactic acid, muriatic acid, and lime. A portion of it was taken and freed from its lime by means of oxalic acid. This portion was then saturated By means of this solution the remainwith carbonate of silver. der of the liquid was freed from muriatic acid. Finally, the lime was thrown down by means of oxalic acid, so that nothing remained but lactic acid dissolved in water. To get rid of a small portion of oxalate of lime which it may hold in solution, it is proper to evaporate it to dryness and redissolve it in water.

When oatmeal, rice, and several other vegetable bodies, are mixed with water, and left to spontaneous fermentation, they acquire an acid taste and smell. The acid thus formed was examined by Braconnot, who considered it as a new acid, and

<sup>\*</sup> Ann. de Chim. I. 288.

<sup>+</sup> Ibid. lix. 280.

<sup>‡</sup> Föreläsningar i D'jurkemien, ii. 430. A translation of his account of lactic acid is published in the Phil. Mag. xli. 241.

gave it the name of nanceic acid.\* But Vogel afterwards showed it to be identical with the lactic acid of Scheele.+

Lactic acid when obtained by Braconnot's process (which Characters. consists in saturating the acid with oxide of zinc, and purifying the salt by a double crystallization. The salt is now dissolved in hot water, the oxide of zinc thrown down by barytes water, and the barytes by sulphuric acid) is colourless. But when the process of Scheele or Berzelius is adopted it has a brownish yellow colour, and a sharp sour taste, which is much weakened by diluting the acid with water. While cold it has no smell, but when heated it acquires a sharp sour odour, not unlike that of sublimed oxalie acid. It does not crystallize, but when evaporated to dryness forms a smooth varnish which gradually attracts moisture from the air. It dissolves readily in alcohol. When heated it boils, emits a sour smell, and leaves a bulky charcoal not easily burnt. When distilled it gives out empyreumatic oil, water, acetic acid, carbonic acid, and inflammable All the salts which it forms with bases are soluble in water, and hardly any of them can be made to assume a crystallized form.

This acid obviously differs from acetic acid in being less volatile. But whether this difference be not owing to some foreign substance combined with acetic acid has not been determined. The lactates described by Berzelius as existing in all animal fluids, have not been sufficiently examined to make their nature certain.

#### 2. Caseic Acid.

This is a name given to a substance formed by Proust, by How obtainsubjecting the curd of milk to the putrefactive fermentation, and which he considered as a peculiar acid. Curd was allowed to putrefy under water at a temperature of about 50°. In about 14 days' time the water will be found to hold in solution phosphate, acetate, and caseate of ammonia, The water is renewed from time to time till the putrefying curd gives out no more of these substances. The watery liquids are evaporated to the consistence of a syrup, which is mixed with alcohol, and the mixture left for some time undisturbed, and the whole is then thrown on the filter. A white substance remains on the filter, to which Proust gave the name of caseic oxide. The alcoholic liquid contains the caseate of ammonia. It is subjected to dis-

<sup>\*</sup> Ann. de Chim, lxxxvi. 86.

<sup>†</sup> Annals of Philosophy, xii. 391.

tillation to get rid of the alcohol. The residue is boiled with water and carbonate of lead, which disengages all the ammonia. The liquid being now filtered is exposed to the action of a current of sulphuretted hydrogen gas to throw down the lead. It is again filtered and concentrated to drive off the acetic acid which it contains. The liquid thus treated consists, according to Proust, of a solution of caseic acid in water.\*

Characters.

This acid is described as a light yellow syrup, which when heated, passes into a horny, translucent, yellow matter, having a sour, bitter, and cheesy taste, and easily soluble in water. According to Braconnot, who has repeated the experiments of Proust, this substance owes its acid properties to a quantity of acetic acid which it contains. But it consists chiefly of various animal matters. One of the most remarkable of which (the caseic oxide of Proust) he has called aposepedine It is mixed with some resin, some oil, and acetate of potash, muriate of potash, and acetate of ammonia.+

It would appear from this that caseic acid is not a peculiar acid, but merely the acetic disguised by a quantity of foreign matter, which retards its volatility. In this respect it resembles lactic acid.

#### 3. Fibric Acid.

How obtain-

I give this provisional name to an acid substance obtained by M. Peretti by the following process: The muscular flesh of an animal is digested in cold water, and the water evaporated to the consistence of a syrup. This matter is digested in strong alcohol, and the solution being set aside for some days in a close vessel, some small needle-shaped crystals make their appearance. These needles redden litmus paper, and when heated give out oil and carbonate of ammonia, with a smell of roast meat. They dissolve easily in water and alcohol, and may be mixed with sulphates and nitrates without undergoing decomposition.‡

These facts are scarcely sufficient to determine the real nature of these crystals. They consist probably of an alkaline super-lactate.

#### SECTION II. - OF FORMIC ACID.

History.

This acid is first mentioned in the Philosophical Transactions for 1671, in a paper by Mr. Ray, giving an account of the

<sup>\*</sup> Ann. de Chim. et de Phys. x. 29.

<sup>†</sup> Ibid. xxxvi. 165.

<sup>1</sup> Jour. de Pharm. xii. 274.

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observations of Mr. Halse, and the experiments of Mr. Fisher, on the acid juice which is spontaneously given out by ants, and which they yield when distilled.\* Mr. Fisher compares this liquor with vinegar, but points out some differences between them. Scarcely any addition was made to these facts till Margraff published a dissertation on the subject in the Berlin Memoirs for 1749, in which he describes the method of obtaining the formic acid from the formica rufa, or red ant, and points out its properties with his usual precision and method.+ A new dissertation was published on the same subject by Messrs. Arvidson and Oehrn in 1782, in which the discoveries of Margraff were confirmed, and many new particulars added. Hermbstadt's paper on the same subject appeared in Crell's Annals for 1784. His researches were directed chiefly to the purification of the formic acid. He demonstrated that the juice of ants contained several foreign bodies, and among others, that a portion of malic acid might be detected in it. Richter published experiments on formic acid about the year 1793, pointing out a method of procuring it in a very concentrated state.; Deveux soon after examined it, and found it analogous to the acetic acid. This opinion of the French chemist was confirmed in 1802, by Fourcroy and Vauquelin, who published a dissertation on ants, and concluded from their experiments, that the formic acid is nothing else than a mixture of the acetic and The opinion maintained by these celebrated malic acids. philosophers induced Suersen to examine the subject by expe-This chemist, in an elaborate dissertation on formic acid, published in 1805,¶ shows that most of the facts pointed out by Fourcroy and Vauquelin had been already ascertained by preceding chemists; that the experiments which they detail were not sufficient to warrant their conclusions; that formic acid, when properly prepared, contains no malic acid; and that it possesses properties different from the acetic. Gehlen was induced to resume the examination of this acid, by some observations which I made upon it in a former edition of this work. He published an elaborate dissertation on it in 1812, in which he compares the properties of formic acid with those of acetic acid, and points out the peculiar characters of formic acid with

<sup>\*</sup> Phil. Trans. v. 2063. + Margraff's Opusc. i. 291. + Gehlen, iv. 7.

<sup>§</sup> Fourcroy, x. 491; Eng. Trans. I have not seen either the dissertation of Richter or Deyeux.

<sup>||</sup> Phil. Mag. xv. 118.

great clearness and precision.\* Since that time it has been analyzed by Berzelius, and an artificial method of preparing it has been discovered by Dobereiner.

How obtained. The simplest method of procuring formic acid in a state of purity is that of Margraff as corrected by Richter. Suersen accordingly had recourse to it. This method is as follows: Infuse any quantity of ants in about thrice their weight of water, put the mixture into a silver or tinned copper still, and draw off the water by distillation as long as it continues to come over without any burnt smell; for the distillation must be stopped as soon as that smell begins to be perceived. Saturate the water in the receiver with carbonate of potash, and evaporate to dryness. Mix the white mass thus obtained with as much sulphuric acid, previously diluted with its weight of water, as is sufficient to saturate the potash. Introduce the mixture into a retort, and distil slowly to dryness. The liquid which comes over into the receiver is to be again rectified by a very moderate heat, to get rid of any portion of sulphuric acid that may be present.

Gehlen, to be still more certain of the purity of his formic acid, saturated the acid prepared by the above process with carbonate of copper, and by the requisite evaporation, separated the formate of copper in crystals. He mixed in a retort 13 ounces of these crystals with 8 ounces 310 grains of sulphuric acid of the specific gravity 1.864 and distilled. He obtained 6 ounces 410 grains of formic acid in a state of purity.

Dobereiner discovered that if we mix together in a large retort one part of crystals of tartaric acid,  $2\frac{1}{2}$  parts of deutoxide of manganese, and  $2\frac{1}{2}$  of sulphuric acid of the specific gravity 1.85, previously diluted with twice its weight of water, and apply heat, much carbonic acid gas is disengaged, and the matter in the retort swells up and has a great tendency to run over. After the disengagement of gas is at an end, if we distil over the liquid we obtain dilute formic acid, which may be concentrated by saturating it with potash or soda, and mixing the formate with the requisite quantity of sulphuric acid and distilling.

Wöhler has found that the process succeeds equally if we substitute starch for tartaric acid. And Liebeg even affirms that many other organic bodies may be substituted for tartaric acid without injuring the process.

Properties.

It has a sharp sour taste and cannot be crystallized, even by

<sup>\*</sup> Schweigger's Journal, iv. 1. + Gilbert's Annalen, lxxi. 107.

the application of artificial cold. Its specific gravity at the temperature of 68° is 1·1168,\* while that of the most concentrated acetic acid does not exceed 1·08, and It contains 19·66 per cent. of water. When mixed with its own weight of pure water its specific gravity becomes 1·06. And if we add twice as much water it becomes 1·0296.

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Dobereiner has ascertained that when mixed with anhydrous sulphuric acid it undergoes decomposition, because it cannot subsist without water or a base. It is converted into carbonic composition. oxide gas and water. From the proportion of carbonic oxide gas evolved, he concluded that it consists of

3 atoms oxygen	•	•	<b>3</b>
2 atoms carbon			1.5
1 atom hydrogen	•	•	0.125
	_		
			1.695

4.625

so that it differs from oxalic acid simply by containing an atom of hydrogen, while oxalic acid contains only 3 atoms of oxygen and 2 atoms of carbon.

This corresponds very well with the analysis of Berzelius, who found its constituents

Hydrogen	•	•	2.84
Carbon .	•	•	$32 \cdot 40$
Oxygen .	•	•	64.76

100.00+

For this is equivalent to

1.05 atom hydrogen2.001 atoms carbon3 atoms oxygen

almost coinciding with the theoretical numbers. The analysis of Dr. Gobel agrees also with this very nearly.‡ There cannot be the least doubt then, that the atomic constitution of this acid is as has been stated, and that its atomic weight is 4.625.

Formic acid has a considerable resemblance to acetic; but they differ in some particulars, particularly when combined with bases. Very dilute formic acid is said to undergo spontaneous decomposition like vinegar. But I have preserved for several years, without any alteration, formic acid prepared by Dobereiner's process, and in a rather dilute state, though much stronger than vinegar.

<sup>\*</sup> Schweigger's Jour. iv. 14. † Annals of Philosophy, ix. 107. † Schweigger's Jahrbuch, ii. 344.

### SECTION III .- OF MELLITIC ACID.

History.

There is a mineral of a honey-yellow colour which is found in small solitary crystals among the layers of wood-coal at Arten in Thuringia. At first sight it has some resemblance to amber; but Werner recognised it as a peculiar substance about the year 1790, and gave it the name of honigstein (honey-stone), which foreign mineralogists converted into mellite. This mineral is very rare. Hitherto indeed it has been found only in Thuringia and in Switzerland.\*

Mellite has usually a honey-yellow colour, but sometimes a straw yellow. It is always crystallized in octahedrons, but they are rarely entire; sometimes indeed almost the whole of one of the pyramids is wanting. Their surface is generally smooth and brilliant, and interiorly they have a glassy lustre. They are semitransparent, brittle, soft, and easily reduced to powder. When pounded, they assume a yellowish-gray colour. Their specific gravity is about 1.550.+

Mineralogists soon discovered that mellite is partly combustible; but they did not agree about its component parts. Lampadius; and Abich undertook its chemical analysis about the same time.

But the results of their analyses differed so much from each other, that little confidence could be placed in either. Besides, it was evident from the way in which their experiments were conducted, that the original component parts of mellite had been altered by fire. Klaproth analyzed it in 1799, and ascertained it to be a compound of alumina and a peculiar acid, to which he gave the name of mellitic. And this analysis was soon after confirmed by Mr. Vauquelin. In the year 1826 M. Wöhler subjected this acid to a new examination, and has added several interesting facts to those which had been previously determined.\*\*

Hitherto mellitic acid has been found only in the mellite. It may be procured from that mineral by the following process: reduce the mellite to powder, and boil it in about 72 times its weight of water. The acid combines with the water, and the alumina separates in flakes. By filtering the solution, and evaporating sufficiently, the mellitic acid is obtained in the

<sup>\*</sup> Brochant's Mineralogy, ii. 75.

<sup>‡</sup> Crell's Annals, 1797, ii. 10.

<sup>∦</sup> Beitrage, iii. 114.

<sup>\*\*</sup> Poggendorf's Annalen, vii. 325.

<sup>+</sup> Klaproth's Beitrage, iii. 115.

<sup>§</sup> Ibid. p. 16.

<sup>¶</sup> Ann. de Chim. xxxvi. 203.

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This was Klaproth's process. But Wöhler state of crystals. on repeating it found that the mellitic acid was not free from alumina. He employed the following process for procuring this acid in a state of purity: Mellite reduced to a fine powder was digested in a solution of carbonate of ammonia, and the liquid, after it had taken up all the mellitic acid, was boiled till all the excess of ammonia was driven off. It was then filtered and evaporated till the mellate of ammonia was obtained in crystals. The pure crystals were dissolved in water and precipitated by acetate of lead. The precipitate being edulcorated was mixed with water, through which a current of sulphuretted hydrogen gas was passed to throw down the lead. The mellitic acid dissolves in the water, and is obtained in a state of purity by filtration.

The liquid obtained in this way being concentrated to the consistence of a syrup did not crystallize, but by continuing the evaporation the acid remained behind in the state of a white powder. Being dissolved in alcohol and left to spontaneous evaporation, the mellitic acid crystallized in very fine needles arranged in the form of stars.

Mellitic acid has a very sour taste, is not altered by exposure Properties to the air, is very soluble in water and alcohol, and bears a pretty high temperature before it is charred. When sublimed in a glass tube a crystalline fusible matter is obtained, which possesses peculiar properties, and has obtained the name of pyromellitic acid. During this sublimation no smell of empyreumatic oil is observed, as usually happens when organic bodies are exposed to a temperature sufficiently high to produce volatilization.

Sulphuric acid, though in a concentrated state, produces no alteration on mellitic acid. It dissolves the acid by a boiling heat, but no alteration is produced in its colour, and the sulphuric acid may be distilled off leaving the mellitic acid unaltered.

Nitric acid, even when assisted by heat, neither dissolves nor alters mellitic acid. In this respect it bears a striking resemblance to oxalic acid.

When a solution of mellitic acid in absolute alcohol is boiled for some time, it would appear from the observations of Wöhler that the nature of the acid is quite altered. When evaporated to the consistence of a syrup it becomes dark brown, and a sour tasted matter remains resembling resin, and like it insoluble in water, though it communicates a sour taste to that

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liquid. When water is left upon this matter for some time a white tasteless substance remains which burns easily with flame like resin, leaving charcoal, but yielding no sublimate. It is scarcely soluble in hot water, but very readily soluble in alcohol. The solution reddens litmus paper. It dissolves also very readily in liquid ammonia.

Atomic weight.

From the analysis of mellate of alumina by Wöhler, its constituents appear to be

Mellitic ac	eid		•	41.4
Alumina		•	, •	14.5
Water	•	•	•	44.1
mivalent to			<b>4</b> ·	100.0

Now this is equivalent to

Mellitic aci	d	•	•	6.424
Alumina	•	•	•	2.25
Water				6.842

2.25 is the weight of an atom of alumina, 6.842 is very near 6.75, the weight of 6 atoms of water, therefore 6.624 must be very nearly the weight of an atom of mellitic acid. We may therefore take 6.5 as affording a near approximation to the true atomic weight of this acid.

From the great permanence of this acid, and its resemblance in many particulars to oxalic acid, it is highly probable that like that acid it contains no hydrogen, but is a compound of carbon and oxygen. Oxalic acid is a compound of 2 atoms carbon and 3 atoms oxygen. Is it not probable that mellitic acid is a compound of

2 atoms carbon	•	•	1.5
5 atoms oxygen	•	•	5
			6.5

This can only be determined by an analysis of mellitic acid. Should it turn out to be free from hydrogen, it will require hereafter to be placed among the acids with a simple base, and next to oxalic acid, to which it has so striking an analogy.

The salts which this acid forms with bases have received the name of mellates.

### SECTION IV .-- OF TARTARIC ACID.

History.

Tartar, or cream of tartar, as it is commonly called, when pure, has occupied the attention of chemists for several centuries. Duhamel and Grosse, and after them Margraff and Rouelle the

younger, proved that it was composed of an acid united to potash; but Scheele was the first who obtained this acid in a separate state. He communicated his process for obtaining it to Retzius, who published it in the Stockholm Transactions for 1770. It consisted in boiling tartar with chalk, and in decomposing the tartrate of lime thus formed by means of sulphuric acid.

The process employed at present for obtaining tartaric acid, Preparation. which is the same with that of Scheele, is the following: dis-

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solve tartar in boiling water, and add to the solution powdered chalk till all effervescence ceases, and the liquid does not redden vegetable blues. Let the liquid cool, and then pass it through a filter. A quantity of tartrate of lime (which is an insoluble white powder) remains upon the filter. Put this tartrate, previously well washed, into a glass cucurbite, and pour on it a quantity of sulphuric acid equal to the weight of the chalk employed, which must be diluted with water. Allow it to digest for 12 hours, stirring it occasionally. phuric acid displaces the tartaric; sulphate of lime remains at the bottom, while the tartaric acid is dissolved in the liquid part. Decant off this last, and try whether it contains any sulphuric acid. This is done by dropping in a little acetate of lead; a precipitate appears, which is insoluble in acetic acid if sulphuric acid be present, but soluble if it be absent. If sulphuric acid be present, the liquid must be digested again on some more tartrate of lime; if not, it is to be slowly evaporated, and about one-third part of the weight of the tartar employed is obtained of crystallized tartaric acid.

Lime may be substituted for chalk in this process. case the decomposition of the tartar is complete; whereas by Scheele's method, the excess of acid only combines with the chalk; but when lime is used, the whole tartrate of lime by no means separates. A considerable portion is retained in solution by the potash of the tartar now disengaged. If the liquid be evaporated, this portion appears under the form of a transparent jelly. By exposure to the air the potash attracts carbonic acid, which unites to the lime, while the tartaric acid combines again with the potash. To obtain the potash in a state of tolerable purity, the best method, according to Vauquelin, to whom we are indebted for these observations, is to evaporate to dryness, and heat the residue to redness. By lixiviating the mass, the potash will be obtained in a state of considerable purity.\*

The crystals of this acid are usually so irregular that it is

<sup>\*</sup> Ann. de Chim. xlvii. 147.

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difficult to refer them to any regular figure. M. Peclet considers them as six-sided prisms, four of the solid angles or edges of which are of 129° and the other two of 102°.\* Mr. Brooke considers the primary form as an oblique rhombic prism. The contiguous two faces of the prism are inclined to each other at angles of 88° 30′, and the base of the prism makes with either of the lateral faces an angle of 97° 10′.† No cleavage has been perceived indicating the direction of the primary faces.

Properties.

Crystallized tartaric acid is white, and very firm, and is but imperfectly transparent. It may be exposed to the air for any length of time without undergoing any change. When heated a few degrees above 212° it melts and remains limpid and transparent like water. At 250° it boils without losing its transparency or becoming coloured. If the boiling be continued for a short time only it does not lose above 4 per cent. of its weight. On cooling it concretes again into a hard semitransparent mass, very much resembling a quantity of white sugar that has been melted at the same temperature. By this process the nature of the acid is changed. It now deliquesces when exposed to the air.

Boiling water dissolves twice its weight of this acid. It is soluble also in alcohol. A dilute aqueous solution gradually undergoes spontaneous solution, being covered with a mucous coat; but I have kept a concentrated solution for years without any change. Nitric acid converts this acid into oxalic, while concentrated sulphuric acid converts it into acetic acid.

Composition.

The crystals contain water as a constituent, but no water can be driven off by heat. However, when the acid is combined with a base, especially with oxide of lead, and the salt is heated, the water is driven off, and nothing remains but the anhydrous acid united to the oxide of lead. In this way Berzelius determined the composition of the crystals to be

Anhydro	ous a	cid	•	•	88.15
Water	•	•	•	•	11.85
					100.001

- \* Ann. de Chim. et de Phys. xxxi. 78. + Ann. of Phil. (2d series), vi. 118.
- † His experimental results were

Acid . . 88.5 Water . . 11.5

100.0

The numbers in the text were derived from theoretic considerations. See Ann. de Chim. lxxxi. 295.

Now, if we consider the water as equivalent to one atom, we obtain for the atomic weight of tartaric acid 8.368. For 11.85 is to 88.15 as 1.125 to 8.368. Now, the result of the analysis of this acid by Berzelius is as follows:

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Carbon 36.8060 or 4.07 atoms carbon Oxygen 60.1895 or 5 atoms oxygen Hydrogen 3.0045 or 1.996 atoms hydrogen

100.000

This comes very near 4 atoms carbon, 5 atoms oxygen, and 2 atoms hydrogen, which is the constitution of this acid according to the analysis of Prout. Hence its atomic weight is 8.25. I have shown in my "First Principles" (p. 113), by a set of experiments which I consider as decisive, that the true atomic weight of tartaric acid is 8.25, and that it is a compound of

4 atoms carbon . . . 3
5 atoms oxygen . . . 5
2 atoms hydrogen . . . 0.25
8.25\*

The combinations of this acid with bases have received the name of tartrates. Like oxalic acid it has a tendency to unite to many bases in two proportions. Tartaric acid is sometimes used in medicine chiefly in the state of salts. But its great use is by the calico-printers, who thicken it with gum or roasted starch, and apply it to those parts of a piece of calico previously dyed red or blue as are to be rendered colourless by means of chloride of lime, or bleaching powder. The tartaric acid combining with the lime sets the chlorine at liberty, which immediately destroys the colour of the part of the cloth on which the thickened acid has been fixed. For this purpose chiefly it is manufactured in this country in great abundance, and sold at a very low price.

Tartaric acid has a great tendency to combine at once with two bases and form double salts. In consequence of this property it prevents antimony from being precipitated as it usually is by water, and even hinders alkaline bodies from precipitating solutions of the metal in acids as they usually do.

<sup>\*</sup> Berzelius has recently admitted this atomic constitution of the acid. His former numbers were 4 C + 5 O + 2½ H. He has shown that tartrate of lime is a compound of 62.7431 oxide of lead, and 37.2569 tartaric acid. See Poggendorf's Annalen, xix. 306.

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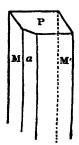
### SECTION V .-- OF VINIC ACID.

The history of the acid to which I give this name is as fol-A maker of tartaric acid at Thann, a small town in Wasgou, observed some years ago, that along with the common acid he obtained portions of another, which was less soluble in water than tartaric. He considered it as oxalic, and endeavoured to introduce it into commerce under that name. first subjected to an examination by Dr. John, who showed in 1819 that it is a peculiar acid.\* Gay-Lussac and Walchner confirmed these results in 1826.† M. Kestner, a very ingenious manufacturer of sulphuric acid, in Alsace, was kind enough to present me with a specimen of this acid in 1827, which enabled me to verify the results of Gay-Lussac, and to determine the atomic weight of this acid, and a few of the salts which it forms with bases. During the course of the summer of 1830, the nature of this acid occupied the attention of Berzelius, as appears by a notice in Brewster's Journal.‡

Gay-Lussac informs us, that during a journey through the department of the Vosges, in company with Darcet, they visited a manufactory in which tartaric acid was made by decomposing tartrate of lime by means of sulphuric acid, and that the manufacturer put into his hands a quantity of acid crystals obtained during his processes, apparently different from the crystals of tartaric acid.

Properties.

The crystals of this new acid, as I received them, were large;



but had been so much injured by shaking in a phial, that it was impossible to make out the shape. On dissolving them in water, and crystallizing a second time, I obtained doubly oblique four-sided prisms, having one of the edges replaced by the narrow face a. P was inclined upon M or M' at about 75°, and M was inclined to M' at about 68°, measured by a common goniometer.

The specific gravity of the crystals was 1.600 at 60°. It has no smell, dissolves readily in water, has a very sour taste, and reddens strongly vegetable blue colours. At the common temperature of the atmosphere, the crystals of this acid require 5.7 times their weight of water to dissolve them according to Walchner.

When vinic acid, saturated with a base, is mixed with a solu-

<sup>\*</sup> Handworterbach der Chemie, iv. 125.

<sup>+</sup> Schweigger's Jahrbuch, xviii. 381, and xix. 238.

<sup>#</sup> Brewster's Journal (new series), iii. 289; also in Poggendorf's Ann. xix. 319.

tion of muriate of lime, a white precipitate falls, which is not the case with tartaric acid. But like tartaric acid it forms a white crystalline precipitate when dropt in excess into a solution of potash or its carbonate.

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When heated with deutoxide of manganese and sulphuric acid, it gives out much carbonic acid and some acetic acid, but no formic acid seems to be formed. When heated it burns, and if distilled it gives out much acidulous water, and leaves a light bulky coal.

Gay-Lussac states the atomic weight of this acid to be almost composition. the same as that of tartaric acid. And Berzelius states that it is exactly the same. I analyzed the vinate of lime, which is a white insoluble powder, and found its constituents

1 atom vinic acid	•	•	<b>8·5</b>
1 atom lime .	•	•	3.5
2 atoms water	•	•	2.25

14.25

This result was corroborated by an analysis of vinate of lead, also a white insoluble powder, which I found composed of

1 atom vinic acid	•	•	8.5
1 atom oxide of lead	•	•	14
1 atom water .	•	•	1.125
			20.025

According to these analyses the atomic weight of this acid is 8.5. This is a little higher than the atomic weight of tartaric. But as I did not make a rigid comparison between the two acids, I do not consider my analyses as sufficiently rigid to settle the point. Being ignorant of the number which Berzelius has adopted for the atomic weight of tartaric acid, I cannot judge how near my determination comes to that of Berzelius.

I found the crystals of vinic acid composed of

1 atom acid		•	•	8.5
2 atoms water		•	•	2.25
	-			

10.75

Thus they differ in their composition from the crystals of tartaric acid.

Should the atomic weight of this acid turn out the same as that of tartaric acid, we will be obliged to conclude that the atoms of which both are composed are the same. They would then be in the same predicament as phosphoric and pyrophosphoric acid.

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SECTION VI. -- OF PYROTARTARIC ACID.

History.

The salt called tartar separates from wine while in the cask, and is afterwards purified by solution in water and subsequent evaporation. This salt occupied the attention of chemists very much from the time of Paracelsus, who first brought it into vogue. It was considered as an acid salt of a peculiar nature. The potash which constitutes its base was easily discovered by subjecting the salt to combustion. But the efforts of chemists to obtain the acid which it manifestly contained were long unsuccessful. When tartar was distilled in a retort, an acidulous liquid was obtained; but it was manifestly different from the acid in tartar, as tartar was not formed when it was united At last in 1770, Scheele discovered a process by to potash. which pure tartaric acid could be obtained from tartar. properties being manifestly different from that of the acid obtained by distilling tartar, as far as could be collected from the rude experiments of the Dijon Academicians,\* the French chemists when they contrived the new chemical nomenclature distinguished them by the names of tartarous and pyrotartarous acids; which were afterwards changed into those of tartaric and pyrotartaric acids.† In the year 1799 a set of experiments was published by Fourcroy and Vauquelin on pyromucous, pyrotartarous, pyrolignous acids, the object of which was to prove, that these acids are merely the acetic disguised by some empyreumatic oil, with which it has combined. This conclusion appears to have been acquiesced in by chemists without examination; though the proofs as far as regards the pyrotartaric acid are far from satisfactory; till Gehlen called it in question in 1806, affirming that pyrotartaric acid differs essentially from acetic, and stating some characters by which they could be easily distinguished.§ This induced Fourcroy and Vauquelin to repeat their experiments in 1807. was a tull confirmation of the opinion of Gehlen.

Preparation.

Pyrotartaric acid may be obtained by the following process: Distil a quantity of tartar in a resort. Saturate the acid liquid

<sup>\*</sup> Elements de Chymie de l'Academie de Dijon, iii. 55.

<sup>†</sup> It was Morveau, in the first volume of the chemical part of the Encyclopædie Methodique, published in 1786, that first drew the attention of chemists to pyrotartaric acid, and endeavoured to characterize it as a peculiar acid. His characters were inaccurate, because he had never obtained it in a state of purity.

<sup>‡</sup> Ann. de Chim. xxxv. 161.

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in the receiver with potash, separate the salt by crystallization, and purify it by repeated solutions and crystallizations. Mix this salt with diluted sulphuric acid, and distil in a retort. An acid liquid passes over, and towards the end of the process a white sublimate rises and attaches itself in scales to the top of the retort. This sublimate is pyrotartaric acid. When the acid liquor in the receiver is subjected to spontaneous evaporation it deposites crystals of pyrotartaric acid.

The taste of pyrotartaric acid is extremely acid. When Properties. heated it melts, and sublimes in a white smoke, without leaving any residue. It dissolves readily in water, and crystallizes again when subjected to spontaneous evaporation. It does not precipitate acetate of lead nor nitrate of silver; but it precipitates nitrate of mercury. Some time after it has been mixed with acetate of lead, needleform crystals make their appearance.

When combined in excess with potash, no salt similar to tartar is formed. In this state it instantly forms a precipitate when dropped into acetate of lead. Pyrotartrate of potash is soluble in alcohol. It does not precipitate the salts of barytes and lime, as tartrate of potash does.\*

### SECTION VII. -- OF CITRIC ACID.

Chemists have always considered the juice of oranges and History.

lemons as an acid. This juice contains a quantity of mucilage and water, which renders the acid impure, and subject to spontaneous decomposition. Mr. Georgi took the following method to separate the mucilage: He filled a bottle entirely with lemon-juice, corked it, and placed it in a cellar: in four years the liquid was become as limpid as water, a quantity of mucilage had fallen to the bottom in the form of flakes, and a thick crust had formed under the cork. He exposed this acid to a cold of 23°, which froze a great part of the water, and left behind a strong and pretty pure acid.† It was Scheele, how-

His process, which is still followed, is this: Saturate lemon juice, while boiling, with powdered chalk. A white powder falls to the bottom, which is lime combined with citric acid. Separate this powder, and wash it with warm water till the

ever, that first pointed out a method of obtaining this acid perfectly pure, and who demonstrated that it possesses peculiar

properties.

<sup>\*</sup> Ann. de Chim. lxiv. 42.

<sup>. +</sup> Kongl. Vetenskaps Academiens Handlingar for 1774, p. 245

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water passes off colourless. Then pour upon it as much sulphuric acid as will saturate the chalk employed, having previously diluted it with six times its weight of water. Boil the mixture for some minutes, and pass it through a filter to separate the sulphate of lime. The liquid is then to be evaporated to the consistence of a syrup, and set aside to cool. A number of crystals form in it: these are citric acid.\*

Mr. Scheele advises the use of an excess of sulphuric acid in order to ensure the separation of all the lime; but according to Dizé, this excess is necessary for another purpose.† A quantity of mucilage, he thinks, still adheres to the citric acid in its combination with lime, and sulphuric acid is necessary to decompose this mucilage.

Proust, who published a memoir on the preparation of citric acid in the Journal de Physique for 1801,‡ has shown that when too much sulphuric acid is employed, it acts upon the citric acid, chars it, and prevents it from crystallizing. This error is remedied by adding a little chalk. This chemist found, that four parts of chalk require for saturation 94 parts of lemon juice. The citrate of lime obtained amounted to  $7\frac{1}{2}$  parts. To decompose this, 20 parts of sulphuric acid, of the specific gravity 1·15, were necessary.

Properties.

The crystals of this acid are of a very irregular figure. They are prisms of 6, 8, or 10 sides, terminated at either extremity by an indefinite number of faces. Mr. Brooke has shown that the primary form is a right rhombic prism, whose faces make angles of 101° 30′.§ They are not altered by exposure to the air. Their specific gravity is 1.617. Their taste is exceedingly acid, and even excites pain; but when the acid is properly diluted with water, the acidity is pleasant. These crystals contain combined water; and, therefore, are in the state of a hydrate. According to the analysis of Berzelius, || they are composed of

Real acid	•	•	82
Water	•	•	18
I have shown that they consis	t o£		
1 atom acid	•	•	7.25
2 atoms water	•	•	2.25
			9.50

<sup>\*</sup> Scheele, ii. 203.

<sup>†</sup> Jour. de Phys. lii. 366.

Ann. de Chim. lxxxii. 297.

<sup>†</sup> Nicholson's Journal, ii. 43.

<sup>§</sup> Annals of Phil. (2d series), vi. 119.

<sup>¶</sup> First Principles, ii. 121.

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This water cannot be driven off by heat. When their temperature is raised they melt and then become yellow or brown, and form a thick syrup which cannot be crystallized. 100 parts of the acid, when kept at such a temperature as to be reduced to the state of a white powder without undergoing decomposition, lose about 7 per cent. of water. This approaches to the third part of the whole water contained in the acid. Indeed I have determined by actual experiment, that the loss of weight is just one-third of the water.\*

Citric acid is exceedingly soluble in water. According to Vauquelin, 100 parts of it require only 75 parts of water. Boiling water dissolves twice its weight of it.† This solution may be kept a long time in close vessels; however, it at last putrefies, and is decomposed.

Neither oxygen gas nor the simple combustibles or incombustibles produce any effect upon it. It is capable of oxidizing iron, zinc, tin. It does not act upon gold, silver, platinum, mercury, bismuth, antimony, arsenic.

It combines with alkalies, earths, and metallic oxides, and forms salts known by the name of citrates.

The action of none of the acids on it has been examined, if we except that of the sulphuric and nitric. Sulphuric acid, when concentrated, converts it into acetic acid. 

Scheele said that he could not convert it into oxalic acid by means of nitric acid, as he had done several other acids: but Westrumb affirms, that this conversion may be effected; and thinks that Scheele had probably failed from having used too large a quantity of nitric acid, by which he had proceeded beyond the conversion into oxalic acid, and had changed the citric acid into vinegar; and in support of his opinion, he quotes his own experiments; from which it appeared that, by treating 60 grains of citric acid with different quantities of nitric acid, his products were very Thus with 200 grains of nitric acid he got 30 grains of oxalic acid; with 300 grains of nitric acid he obtained only 15 grains of the oxalic acid; and with 600 grains of nitric acid no vestige appeared of the oxalic acid. On distilling the products of these experiments, especially of the last, he obtained vinegar mixed with nitric acid. The experiments of Westrumb have been confirmed by Fourcroy and Vauquelin; who, by treating citric acid with a great quantity of nitric acid, con-

<sup>\*</sup> First Principles, ii. 122.

verted it into oxalic and acetic acids. The proportion of the first was much smaller than that of the second.

Constituents

According to the analysis of Berzelius (corrected a little by theoretic views), citric acid is composed of

Hydrogen	•	•	•	3.42
Carbon	•	•	•	41.84
Oxygen	•	•	•	54.74
				100.00*
This is equivalent to				
2 atoms hydr	ogen		•	0.25
4 atoms carbo	on		•,	. 3
4 atoms oxyg	en	_		4

**7·2**5

Now as these atoms give us the true atomic weight of citric acid, there can be no doubt that the result just given represents the true atomic composition of this acid. My own analytical results, so far as they go, coincide with those of Berzelius.†

#### SECTION VIII. -- OF PYROCITRIC ACID.

History.

This acid was discovered by M. Lassaigne,‡ to whom we are indebted for all the facts respecting it hitherto ascertained.

When citric acid is distilled in a glass retort it fuses, water passes over, it then becomes yellow, and the colour deepens more and more, while a white vapour passes over and condenses in the receiver. The product of the distillation is a colourless liquid swimming uppermost, and an amber-coloured oily liquid at the bottom of the receiver. The watery liquid has an acid taste, and the amber liquid contains a good deal of acid which it gives out to water. To obtain the acid contained in the liquid by saturating it with lime, and evaporating the liquid, a solid salt was obtained, which dissolved in water, and gave no smell of acetic acid when treated with sulphuric acid.

Two methods of separating the pyrocitric acid from the lime were taken: 1. The lime was thrown down by oxalic acid; 2. The pyrocitrate of lime was decomposed by acetate of lead. An insoluble precipitate of pyrocitrate of lead fell, which was washed and decomposed by sulphuretted hydrogen gas.

Properties.

Pyrocitric acid thus obtained is white, without smell, having

<sup>\*</sup> Annals of Philosophy, v. 93. † See First Principles, ii. 123.

<sup>‡</sup> Ann. de Chim. ct de Phys. xxi. 100.

an acid and slightly bitterish taste, and not easily reduced to regular crystals, and assuming usually the state of a white mass, composed of fine needles interlaced together.

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When thrown upon a hot body it melts, and is converted into white acrid vapours, leaving a trace of coal. Distilled in a retort it gives off a yellowish sour-tasted oil, and is partly decomposed. It is very soluble in alcohol; and water at the temperature of 50°, dissolves the third of its weight of it.

Its aqueous solution reddens litmus paper. It neither precipitates lime-water, nor barytes-water, nor any of the metallic solutions tried, except acetate of lead and nitrate of mercury.

With the different bases it forms salts, which have received the name of pyrocitrates.

Lassaigne assures us that its saturating power is precisely Atomic weight. that of citric acid. But from the different analyses of the pyrocitrates which he has given, it is difficult to come to any con-The pyrocitrate of barytes he found composed of clusion.

Pyrocitric acid	•	•	7.43
Barytes	•	•	9.5
The pyrocitrate of lead of			
Pyrocitric acid	•		7.01
Oxide of lead		•	14
While the pyrocitrate of lime	was	compos	sed of
Pyrocitric acid	•	•	6.8
Lime	•	•	3.5*

These three salts give us 7.43, 7.01, 6.8, for the atomic weight of tartaric acid; the mean of which is 7.08, which is below the atomic weight of citric acid. If we were to leave out the analysis of pyrocitrate of lime as uncertain, the mean of the other two would give us 7.22 for the atomic weight of this acid, a result very near that of citric acid. But Lassaigne analyzed it by heating pyrocitrate of lead with black oxide of copper, and obtained for its constituents,

Hydrogen	•	•	9
Carbon	•	•	47.5
Oxygen	•	•	43.5
			100

\* In Lassaigne's paper the salt is said to be composed of Pyrotartaric acid

Lime 66

100

But I suppose the numbers to have been inverted by the printer.

Now the smallest number of atoms which would correspond with the constituents in these proportions is,

1	atom hydrogen	•	•	0.125
$7\frac{1}{2}$	atoms carbon	•	•	5.625
5	atoms oxygen	•	•	5

10.75

This would make the atomic weight of the acid 10.75, a number quite at variance with that resulting from the analysis of the pyrocitrates. It is obvious from this that some of these results are inaccurate, and that new researches are necessary before we can have any accurate knowledge either of the atomic weight or atomic constituents of this acid.

## SECTION IX .- OF MALIC ACID.

History.

This acid, which was discovered by Scheele in 1785, has received the name of malic acid, because it may be obtained in abundance from the juice of apples, in which it exists ready formed. Scheele has given us the following process for extracting it: Saturate the juice of apples with potash, and add to the solution acetate of lead till no more precipitation ensues. Wash the precipitate carefully with a sufficient quantity of water; then pour upon it diluted sulphuric acid till the mixture has a perfectly acid taste, without any of that sweetness which is perceptible as long as any lead remains dissolved in it; then separate the sulphate of lead, which has precipitated, by filtration, and there remains behind malic acid.\*

M. Braconnot has shown that when malic acid is obtained by this process of Scheele, it is contaminated with a mucilaginous matter, intermediate between sugar and gum, which masks all its properties.†

Vauquelin ascertained that it may be extracted, with greater advantage, from the juice of the sempervivum tectorum, or common house-leek, where it exists abundantly, combined with lime. The process which he found to answer best is the following: To the juice of the house-leek add acetate of lead as long as any precipitate takes place. Wash the precipitate, and decompose it by means of diluted sulphuric acid in the manner directed by Scheele.‡

Gay-Lussac has shown that when malic acid is obtained in

<sup>\*</sup> Swedish Trans. and Crell's Annals for 1785.

<sup>†</sup> Ann. de Chim. et de Phys. viii. 149.

<sup>‡</sup> Ibid. xxxiv. 127.

this way, it still retains a quantity of lime, from which it may be freed by evaporating it to the consistence of a syrup, and mixing it with alcohol. Malate of lime is precipitated, and the malic acid remains dissolved in the alcohol.\* But the acid even when thus purified, retains the mucilaginous matter with which it is contaminated when extracted from the juice of apples, as Braconnot has shown.+

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In the year 1815, Mr. Donovan announced the existence of Preparation. a new acid in the expressed juice of the berries of the pyrus aucuparia, to which he gave the name of sorbic acid. His method of procuring this acid was the following:

The berries are to be collected when fully ripe. They are to be first bruised in a mortar, and then squeezed in a linen bag. They yield nearly half their weight of juice of the specific gravity 1.077. This juice is to be strained and mixed with a filtered solution of acetate of lead. Separate the precipitate on a filter, and wash it with cold water. A large quantity of boiling water is then to be poured upon the filter, and allowed to pass through the precipitate into glass jars. After some hours this liquid becomes opaque, and deposites crystals of great lustre and beauty. The matter remaining on the filter has now become hard and brittle. But it may be made to furnish more crystals by the following treatment: Boil it for half an hour with rather more diluted sulphuric acid than is sufficient to saturate the whole lead which it contains. Filter the liquid and treat it again with acetate of lead. The edulcorated precipitate, when treated as before with boiling water, yields an additional crop of crystals. This process may be repeated till almost the whole acid has been obtained united to lead in a crystallized state.

Collect the crystals formed, and boil them for half an hour with 2.3 times their weight of sulphuric acid of the specific gravity 1.090, supplying water as fast as it evaporates, and taking care to keep the mixture constantly stirred with a glass rod. The clear liquor is to be poured off and put into a tall glass jar of small diameter. While still hot, a stream of sulphuretted hydrogen gas is to be passed through it. When the lead is all precipitated the fluid is to be filtered and boiled in an open basin till the sulphuretted hydrogen is disengaged. The liquid now consists of water, holding sorbic acid in solution.‡

<sup>\*</sup> Ann. de Chim. et de Phys. vi. 351.

<sup>†</sup> Ibid. vol. viii. p. 149.

<sup>‡</sup> Phil. Trans. 1815.

M. Braconnot has given us the following process, for extracting this acid from the berries of the pyrus aucuparia, which he recommends as easier than the process of Donovan:

The berries are to be taken before they are ripe, pounded in a marble mortar, and the juice squeezed out by a strong pressure. The juice is to be heated in a capsule, to the boiling temperature, and carbonate of lime is to be thrown in as long as any effervescence continues. Evaporate the liquid to the consistence of a syrup, taking care to skim off the scum in proportion as it collects on the surface. A granular precipitate of sorbate of lime falls, which adheres strongly to the vessel, unless care be taken to stir the liquid from time to time. After an interval of some hours, decant off the syrupy liquid, and wash the precipitate with a little cold water. Then squeeze it in a cloth and dry it. The colour of this salt is fawn, indicating that it is not free from the colouring matter of the berries. Boil it for a quarter of an hour with a quantity of crystallized carbonate of soda equal to it in weight, and a sufficient quantity of water. A double decomposition takes place, and the liquid retains in solution sorbate of soda, mixed with a quantity of colouring matter. This colouring matter is removed by heating the liquid for some time with lime water, or milk of The liquid when filtered becomes quite colourless. current of carbonic acid gas passed through it precipitates the lime retained in solution. The liquid thus freed from colouring matter is to be precipitated by subacetate of lead, and the sorbate of lead may be decomposed, and the acid obtained in solution in water by digesting it with the requisite quantity of dilute sulphuric acid.\* I have repeated this process of Braconnot very exactly; but did not succeed in freeing the acid from the colouring matter. The berries which I employed were fully ripe, while Braconnot's probably were green. Perhaps this may account for the difference between our results.

In the year 1818, Braconnot made a set of experiments on malic acid from the juice of the apple, and from the leaves of the sempervivum tectorum, or house-leeh, and demonstrated that when freed from the mucilaginous matter with which it is usually mixed and disguised, it possesses exactly the properties of sorbic acid.† Hence it follows that sorbic acid is not a peculiar acid, as Donovan supposed; but merely the malic acid of Scheele, in a state of greater purity than that chemist had

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been able to obtain it. Of course we must drop one or other of these two terms, and as Scheele was undoubtedly the first discoverer of this acid, though he did not succeed in procuring it in a state of purity, it seems but fair to retain the name malic acid, which that illustrious chemist originally bestowed on it.

Braconnot obtained pure malic acid from the juice of the house-leek, in the following manner: The expressed juice of the plant was evaporated to the consistence of a syrup, and alcohol being gradually mixed with it, threw down the precipitate usually considered as malate of lime. This precipitate was pressed strongly in a cloth to free it as completely as possible of the saccherine matter with which it was mixed. was then dissolved in water, to which it communicated a brown Sulphuric acid was added to the liquid in such quantity as only partially to decompose the salt, and the liquid was filtered in order to separate the sulphate of lime precipitated. The liquid, which had now a decidedly sour taste, being set aside for 24 hours, deposited a colourless salt, consisting of bimalate of lime. This salt being redissolved and crystallized slowly, formed six-sided flat prisms, terminated by bihedral summits, of the purest white colour. These crystals being dissolved in water were decomposed by sulphuric acid, and in order to get rid of all the sulphuric acid, the filtered liquid was digested over oxide of lead, and the whole being filtered, a current of sulphuretted hydrogen gas was passed through it to thrown down the dissolved lead. It was now evaporated to the consistence of a syrup, and dissolved in alcohol to get rid of some lime and oxide of lead, not separated by the previous processes. The alcoholic solution being evaporated to the consistence of a syrup did not crystallize in 24 hours; but being put into a stove it crystallized completely within the same interval of time. The crystals first formed were groups of small flattened globules of about a line in diameter, and by degrees the whole concreted into an opaque white mass tuberculated on the surface.

Malic acid thus obtained is a white opaque substance, having Properties, an exceedingly sour taste, but destitute of smell, and exceedingly soluble both in water and alcohol.

When dropt into solutions of nitrate of lead, nitrate of silver, or nitrate of mercury, it occasions no precipitate. In acetate of lead it throws down a white precipitate soluble in acetic acid, and even in boiling water. When acetate of lead is dropt into this acid, diluted with water, a copious white precipitate falls,

which gradually redissolves in the liquid, and is slowly converted into very fine silky crystals, having a great deal of lustre. When these crystals are boiled in water they partially dissolve, but the greatest part of them melt into a resinous looking matter which may be drawn out into the threads, but which becomes brittle as soon as the temperature sinks.

Neither lime water nor barytes water occasion any precipitate when dropt into this acid.

The malates of potash and soda are incrystallizable, deliquescent, and insoluble in strong alcohol. But the bimalates of potash, soda, and ammonia, crystallize.

When saturated with magnesia, or with oxide of zinc, it forms salts, which crystallize with the greatest facility.

Scheele considered the acid produced by treating sugar with a quantity of fuming nitric acid equal to its own weight, and previously diluted with its own weight of water, to be malic acid. But from the experiments of Vogel, there is reason to believe that it constitutes a different and peculiar acid, which requires further examination.\*

Various analyses of malic acid have been made, but the results differ so much from each other that we can only reconcile them by supposing that two different acids have been hitherto constituents confounded under the name of malic acid. And the properties of this acid as they have been hitherto stated, are so vague, that this may very well have been the case. According to Frommherz, malic acid is composed of

Hydrogen	•	•	4.756
Carbon	•	•	$29 \cdot 297$
Oxygen	•	•	65.947
			******

100.000+

This is equivalent to 3.46 atoms hydrogen, 3.59 atoms carbon, and 6 atoms oxygen. Frommherz, therefore, considers it as a compound of

$3^{5}$	atoms	hydrogen		•	•	0.4375
$3\frac{1}{2}$	atoms	carbon		•	•	2.6250
6	atoms	oxygen	•	•	•	6.0000
						-
						9.0625

This would make the atomic weight of the acid 9.0625. He analyzed the malate of lead, and found it composed of

<sup>\*</sup> Gilbert's Annalen, lxi. 233.

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Malic acid	•	•	39·2725 or 9·053	
Oxide of lead	•	•	60·7275 or 14	

100.0000

According to this analysis, the atomic weight of the acid is 9.053; which agrees very nearly with the analytical result obtained by decomposing malic acid.

Dr. Prout likewise subjected the malic acid from the berries of the mountain ash to an analysis, and obtained

Hydrogen		•	•	5.08
Carbon	•	•	•	40.68
Oxygen		•	•	54.24
•				
				100.00

Now the smallest number of atoms that correspond with these proportions is

l atom hydrogen	•	•	0.125
13 atoms carbon	•	•	9.75
13 atoms oxygen	•	•	22.00
			***************************************
			20.275

This would make the atomic weight 22.875, a number utterly irreconcilable with that obtained by Frommherz, from experiments which appear to approach very near the truth. Dobereiner's analysis of the same acids gives quite different results. According to him it is composed of

1 atom hydrogen	•	•	0.125
2 atoms carbon	•		1.5
3 atoms oxygen	•	•	3
			4.625*

This is opviously the constitution of formic acid, which Dobereiner must have somehow substituted for malic acid. The analyses of Braconnot, so far as they go, approach very nearly to those of Frommherz. These facts seem to lead to the conclusion that two different acids have been confounded together under the same name. That one of them has been analyzed by Frommherz, and the other by Prout. But this obscure subject can only be cleared up by future researches.

There are four acids which have been distinguished by peculiar names, but which possess properties so nearly resembling those of malic acid, that in all probability they are merely

<sup>\*</sup> Schweigger's Jour. xxvi. 275.

that acid, disguised by the presence of some foreign matter. I shall give a short account of these acids in this place.

## 1. Fungic Acid.

This acid was found by Braconnet in the Peziza nigra, the Hydnum hybridum and repandum, the Boletus juglandis and pseudo-igniarius, the Phallus impudicus, and the Merulius cartharellus;\* and by Schrader in the Helvella mitra.

How ob-

The method of obtaining it followed by Braconnet was this: The juice of the Boletus juglandis was obtained by pressure, and the dry residue was washed with water. The liquid thus obtained was boiled, and the albumen which had coagulated was separated by the filter. It was then gently evaporated to dryness, and the dry residue was well washed with alcohol. portion left by the alcohol was dissolved in water. lead being dropped into the solution, boletate of lead was thrown down in abundance. This fungate was collected and washed on the filter. This salt being digested with dilute sulphuric acid a brown liquid was obtained containing fungic acid, phosphoric acid, animal matter, &c. Being saturated with ammonia and evaporated, crystals of fungate of ammonia were obtained, which, being redissolved and crystallized and subjected to pressure between folds of blotting paper, were pretty white. These crystals were dissolved in water and the acid again thrown down by acetate of lead, and from the precipitate pure fungic acid was separated by means of dilute sulphuric acid.

The acid thus obtained was colourless, would not crystallize, had a very sour taste, and when evaporated to dryness absorbed moisture from the atmosphere. It does not throw down lime from a solution of the muriate, not even when in the state of fungate of potash. Such are the characters of this acid given by Braconnet, together with a very short account of some of its salts. All these characters will apply to some of the acids that have been described by chemists under the name of malic acid.

## 2. Igasuric Acid.

This is the name by which Pelletier and Caventou have thought proper to distinguish an acid, which exists in St. Ignatius's bean, the fruit of the *strychnos ignatia*, in which they first detected the new alkaline substance to which they gave the name of *strychnine*.

<sup>\*</sup> Ann. de Chim. lxxix. 293, and lxxxvii. 242.

Igasuric acid was obtained in the following manner: The magnesia by means of which the strychnine had been separated from the infusion of St. Ignatius's bean, was washed in cold Preparation. water to deprive it as completely as possible of the colouring matter with which it was mixed. It was then boiled in a great quantity of distilled water to dissolve the igasurate of magne-The solution being concentrated by evaporation, was mixed with acetate of lead. A double decomposition took place, and the igasurate of lead was precipitated in the state of an insoluble powder. This powder was mixed with water, and the lead separated from it by means of sulphuretted hydrogen gas. The igasuric acid dissolves in the water, and may be ob-

tained in a separate state by evaporating that liquid. The only character by which this acid is distinguished from the malic is the property which it has of precipitating copper in the state of a greenish white powder, and by the solubility of its alkaline salts in alcohol.

### 3. Laccic Acid.

This acid was obtained by Dr. John from stick lac.\* process was the following: Stick lac was reduced to powder, and digested in water as long as it communicated any colour. The aqueous solution was evaporated to dryness, and the residue digested in alcohol. The alcoholic solution was likewise Preparation. evaporated to dryness, and the dry residue digested in ether. The ether solution being also evaporated left a syrupy mass of a light yellow colour, which being again dissolved in alcohol, and the solution mixed with water, lets fall a little resin. liquid now contains the laccic acid, united with a little potash and lime, from which it may be separated by precipitating it with lead, and decomposing the laccate by means of a quantity of sulphuric acid, just sufficient to saturate the oxide of lead. Thus obtained, it possesses the following properties:

It is capable of crystallizing. Its colour is wine yellow. Its taste is acid. It is soluble in water, alcohol, and ether.

It throws down lead and mercury from their solutions in acids white. But it does not precipitate lime water, nor the nitrates of silver and barytes.

Whether pure, or combined with a base, it throws down the salts of iron white.

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<sup>\*</sup> Lac is a substance formed by insects in India. Sealing-wax consists chiefly of it.

Its compounds with lime, soda, and potash, are deliquescent and soluble in alcohol.\*\*

Most of these characters would apply equally well to malic acid.

### 4. Solanic Acid.

This is an acid found by Peschier in the fruit of the whole tribe of solanums, especially the berries of the solanum nigrum.

It crystallizes. It forms with potash and soda crystallizable salts. It does not precipitate salts of barytes, lime, magnesia, zinc, iron, or copper, but it throws down salts of lead, mercury, and silver.+

All these properties agree with malic acid, leaving little doubt about the nature of the acid, which exists in the berries of the solanum.

The menispermic acid of Boullay has been ascertained to be malic acid. The same remark applies to the acid detected by Braconnot in the phytological decandra.

### SECTION X .-- OF PYROMALIC ACID.

History.

Vauquelin first observed that when crystallized malic acid is heated, white needles are volatilized at a certain temperature, constituting an acid of a peculiar nature. The same remark was made by Braconnot, who distinguished the new acid by the name of *pyro-malic*. For the fullest account of its properties we are indebted to M. Lassaigne.‡

He distilled 20 grammes of crystallized malic acid in a glass retort with a moderate heat. Pure water first came over, then the acid became coloured, and on augmenting the heat a colourless liquid passed over, having a slightly bituminous odour, and an acidity so strong that it blistered the lips and the tongue. Towards the end of the process a few white needles sublimed. A very bulky charcoal remained in the retort. The acid liquid being evaporated to one-half, yielded prismatic crystals of pyromalic acid.

Properties.

This acid undergoes no alteration when exposed to the air. It melts when heated to 117½°. When allowed to cool it concretes into a mass crystallized in needles diverging from a centre and having a pearly lustre. When thrown upon burning coals a white acid smoke isexhaled, irritating the nostrils and exciting cough, and nothing whatever remains. When it

<sup>\*</sup> Schweigger's Journal, xv. 110. + Jour. de Chim. Medic. iii. 289.

<sup>. ‡</sup> Ann. de Chim. et de Phys. xi. 93.

is distilled in close vessels the greater part sublimes in long needles, though a small portion undergoes decomposition.

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Water of the temperature 50° dissolves about half its weight of this acid. It is very soluble in alcohol. The aqueous solution reddens vegetable blues, and precipitates acetate of lead and nitrate of mercury white. It does not precipitate lime water. When dropt into barytes water a white powder falls, redissolved by the addition of a little water, and after some time little silvery concretions appear on the sides of the vessel, consisting of pyromalate of barytes. This salt, according to Lassaigne, is composed of

Pyrometic acid . . . 100
Barytes . . . 185·142

If we consider this salt as neutral, these numbers give 5·131 as the atomic weight of pyromalic acid.

All these characters resemble so closely those of *pyro-citric* acid, that we can scarcely avoid concluding that the pyrocitric and pyromalic constitute one and the same acid.

Lassaigne examined the white needles which sublimed during the distillation of malic acid. He found their properties quite different from those of pyromalic. They approach very near benzoic acid, but differ in some few circumstances. They are probably entitled to be considered as a new acid.\* These conclusions have been confirmed by Rose.†

#### SECTION XI. -- OF MUCIC ACID.

This acid was discovered by Scheele in 1780. After having History. obtained oxalic acid from sugar, he wished to examine whether the sugar of milk would furnish the same product. Upon four ounces of pure sugar of milk, finely powdered, he poured 12 ounces of diluted nitric acid, and put the mixture in a large glass retort, which he placed in a sand-bath. A violent effervescence ensuing, he was obliged to remove the retort from the sand-bath till the commotion ceased. He then continued the distillation till the mixture became yellow. As no crystals appeared in the liquor remaining in the retort after standing two days, he repeated the distillation as before, with the addition of eight ounces of nitric acid, and continued the operation till the yellow colour, which had disappeared on the addition of the nitric acid, returned. The liquor in the retort contained a white powder, and when cold was observed to be thick.

<sup>\*</sup> Ann. de Chim, et Phys. xi. 97. + Poggendorf's Annalen, vii. 87.

Eight ounces of water were added to dilute this liquor, which was then filtrated, by which the white powder was separated; which being edulcorated and dried, weighed 7½ dr. The filtrated solution was evaporated to the consistence of a syrup, and again subjected to distillation, with four ounces of nitric acid as before; after which, the liquor when cold was observed to contain many small, oblong, sour crystals, together with some white powder. This powder being separated, the liquor was again distilled with more nitric acid as before, by which means the liquor was rendered capable of yielding crystals again, and by one distillation more, with more nitric acid, the whole of the liquor was converted into crystals. These crystals added together weighed five drachms, and were found upon trial to have the properties of the oxalic acid.

Mr. Scheele next examined the properties of the white powder, and found it to be an acid of a peculiar nature, he therefore called it the acid of the sugar of milh.\* It was afterwards called saclactic acid by the French chemists. Fourcroy changed that name into that of mucous acid, because it is obtained by treating gum arabic and other mucilaginous substances with nitric acid. And this name has been since altered to that of mucic acid.

How ob. tained,

Mucic acid may be obtained by the following process: Upon one part of gum arabic, or other similar gum, previously put into a retort, pour two parts of nitric acid diluted with water. Apply a slight heat for a short time, till a little nitrous gas and carbonic acid gas comes over, then allow the mixture to cool. A white powder gradually precipitates, which may be easily separated by filtration. This powder is mucic acid.+ It is not however pure, being mixed with a considerable portion of oxalate of lime, and with about 6 per cent. of a substance which is probably a compound of gum and lime. The oxalate of lime may be separated by digesting the white powder repeatedly in diluted nitric acid. The gummate of lime is separated by dissolving the residual saclactic acid in boiling water, the gummate being insoluble in that liquid. The water on cooling deposits saclactic acid in a state of purity. † If sugar of milk be employed instead of gum, the saclactic acid is obtained at once in a state of purity.

Properties.

Mucic acid thus obtained is under the form of a white gritty powder, with a slightly acid taste.

<sup>\*</sup> Scheele, ii. 69.

<sup>+</sup> Fourcroy, vii. 146.

<sup>‡</sup> Laugier; Ann. de Chim. lxxii. 81.

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Heat decomposes it. When distilled there comes over an acid liquor which crystallizes in needles on cooling, containing pyromucic acid, a red coloured acrid oil, carbonic acid gas, and carburetted hydrogen gas. There remains in the retort a large proportion of charcoal. According to Trommsdorf, an acid in crystals is also obtained, which possesses the properties of succence acid.\*

Mucic acid, according to Scheele, is soluble in 60 parts of its weight of boiling water, but Messrs. Hermbstadt and Morveau found that boiling water only dissolved by the part: it deposited about the part on cooling in the form of crystals.

The solution has an acid taste, and reddens the infusion of turnsol. Its specific gravity, at the temperature of 53.7°, is 1.0015.¶

The compounds which it forms with earths, alkalies, and metallic oxides, are denominated *mucates*. These salts are but very imperfectly known, few chemists having examined them except Scheele. The facts which he ascertained are the following:

With potash it forms a salt soluble in eight parts of boiling water, which crystallizes on cooling. The mucate of soda also crystallizes, and is soluble in five parts of water. Mucate of ammonia loses its base by a moderate heat, while the acid remains behind. The compounds which it forms with the earths are nearly insoluble in water. It scarcely acts upon any of the metals, but it combines with their oxides; it forms salts almost insoluble in water. When poured into the nitrates of silver, mercury, or lead, it occasions a white precipitate. It produces no change on the sulphates of iron, copper, zinc, manganese, nor on the muriates of tin and mercury.\*\*

Three very careful analyses of this acid have been made, the composition, first by Gay-Lussac and Thenard, the second by Berzelius, tand the third by Dr. Prout. The following table exhibits the results obtained by each of these chemists:

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Hydrogen. Carbon. Oxygen.

Gay-Lussac 3.62 + 33.69 + 62.69 = 100

Berzelius 4.72 + 34.72 + 60.56 = 100

Prout 4.94 + 33.33 + 61.73 = 100
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<sup>\*</sup> Ann. de Chim. lxxi. 79. + Phys. Chem. 

‡ Encyc. Method. i. 290.

<sup>§</sup> Scheele. | Ibid. | Morveau, ibid.

<sup>\*\*</sup> Scheele, ii. 76. †† Recherches Physico-chimique, ii. 298.

<sup>#</sup> Annals of Philosophy, v. 179.

I have shown from the analysis of mucate of soda, that the atomic weight of this acid is 13.\* Comparing this with the preceding analyses, it is obviously a compound of

4 atoms hydrogen	•	•	0.5
6 atoms carbon	•	•	4.5
8 atoms oxygen	•	•	8
			13.0

These atomic proportions correspond with

as the true atomic weight of this acid.

T.J.		•	•	3.84
Hydrogen	•	•	•	0.04
Carbon	•	•	•	<b>·34·61</b>
Oxygen	•	•	•	61.55
				100.00

Numbers not deviating much from the mean of the preceding analyses. Were we to admit with Berzelius 5 atoms hydrogen, the atomic weight would be 13·125, and the quantity of hydrogen per cent. would be 4·78. This would suit the analyses of Berzelius and Prout; but would not agree with that of Gay-Lussac and Thenard. I am disposed, therefore, to consider 13

### SECTION XII. -- OF PYROMUCIC ACID.

History.

This acid was obtained by M. Houton Labillardiere, by distilling mucic acid in a retort.† The matter which comes over into the receiver is to be mixed with four times its weight of water, and then evaporated to the requisite degree. The pyromucic acid is deposited in crystals, and more crystals are obtained when the mother liquor is concentrated still farther.

\*Properties,

Pyromucic acid thus obtained melts at the temperature of 266°, and if the heat be continued, sublimes in the form of yellow crystals, which on being dissolved in water, and crystallized, become perfectly white and pure.

Pyromucic acid is white, has an acid taste, and is destitute of smell. It does not deliquesce. It reddens vegetable blues. It is more soluble in hot than in cold water. Alcohol dissolves it more abundantly than water. Most of the salts which it forms are soluble and crystallizable. They have received the name of pyromucates.

Most of the pyromucates are very soluble in water. The

<sup>\*</sup> First Principles, ii. 146. † Ann. de Chim. et de Phys. ix. 365.

only metallic salts which it precipitates are those containing peroxide of iron, protoxide of mercury, and peroxide of tin. Pyromucate of ammonia might be substituted for benzoate or succinate of ammonia for throwing down peroxide of iron from neutral solutions.

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Pyromucate of barytes, according to the analysis of Houton Composition. Labillardiere, is composed as follows:

Acid	•	•	57·7 or	12.98
Barytes	•	•	42.2 or	9.5
-			-	
			99.9	

According to this analysis, the equivalent number for this acid is 12.98 or 13.

When analyzed by means of peroxide of copper, its constituents were found to be

Carbon	•	•	<b>52·118</b>
Oxygen	•	•	45.806
Hydrogen	•	•	2.111
			100.035

The number of atoms coming nearest to these proportions, and to the equivalent number for the acid, as indicated by the composition of pyromucate of barytes, is as follows:

9 atoms carbon	n = 6.75	•	•	51.92
6 atoms oxyge	n = 6	•	•	<b>46·16</b>
2 atoms hydro	gen = 0.25	•	•	1.92
	13.			100.

Now these numbers coincide very nearly with those derived from the actual analysis. Thus the atomic weights of mucic and pyromucic acid are the same, but their atomic constituents are very different. The carbon has greatly increased, while the oxygen and hydrogen has considerably diminished.

# SECTION XIII. OF SUCCINIC ACID.

Amber is a well-known brown, transparent, inflammable History. body, pretty hard, and susceptible of polish, found at some depth in the earth, and on the sea coast of the Baltic and England. It was in high estimation among the ancients both as an ornament and a medicine. When this substance is distilled, a volatile salt is obtained, which is mentioned by Agricola under the name of salt of amber; but its nature was long unknown.

Boyle was the first who discovered that it was an acid.\* From succinum, the Latin name of amber, this acid has received the appellation of succinic acid.

Mr. Pott seems to have been the first chemist who made a set of experiments to ascertain its properties, and who demonstrated that it differs from every other.+

Preparation.

It is obtained by the following process: Fill a retort half-way with powdered amber, and cover the powder with a quantity of dry sand; lute on a receiver, and distil in a sand-bath without employing too much heat. There passes over first an insipid phlegm; then a weak acid, which, according to Scheele, is the acetic; then the succinic acid attaches itself to the neck of the retort; and if the distillation be continued, there comes over at last a thick brown oil, which has an acid taste.

The succinic acid is at first mixed with a quantity of oil. It may be made tolerably pure by dissolving it in hot water, and putting upon the filter a little cotton, previously moistened with oil of amber: this substance retains most of the oil, and allows the solution to pass clear. The acid is then to be crystallized by a gentle evaporation; and this process is to be repeated till the acid be sufficiently pure. Guyton Morveau has shown that it may be made quite pure by distilling off it a sufficient quantity of nitric acid, taking care not to employ a heat strong enough to sublime the succinic acid.

Properties.

The crystals of succinic acid are transparent, white, shining, and of a foliated, triangular, prismatic form: they have an acid taste, but are not corrosive: they redden tincture of turnsol, but have little effect on that of violets.

They sublime when exposed to a considerable heat, but not at the heat of a water-bath. In a sand-bath they melt, and then sublime and condense in the upper part of the vessel; but the coal which remains shows that they are partly decomposed.

One part of this acid dissolves in 96 parts of water at the temperature of 50°, according to Spielman;¶ in 24 parts at the temperature of 52°; and in two parts of water at the temperature of 212°, according to Stockar de Neuforn;\*\* but the greatest part crystallizes as the water cools. According to Roux, however, it still retains more of the acid than cold water

<sup>\*</sup> Boyle abridged by Shaw, iii. 369.

<sup>+</sup> Mem. Berlin. 1753. See an abstract of his paper in Lewis's edition of Neuman's Chemistry, p. 237.

<sup>‡</sup> Bergman's Notes on Scheffer. § Ann. de Chim, xxix. 165. | Pott.

<sup>¶</sup> Inst. Chem. § xii. \*\* De Succino.

is capable of dissolving.\* Two hundred and forty grains of boiling alcohol dissolve 177 of this acid; but crystals again shoot as the solution cools.†

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Sulphuric acid dissolves it with the assistance of heat; but does not appear to decompose it. The same remark applies to nitric acid. Muriatic acid has but little action on it while cold; but when heat is applied, the whole coagulates into the consistence of a jelly.‡

The compounds which this acid forms with alkalies, acids, and metallic oxides, have received the name of succinates. The alkaline succinates are soluble in water. This is the case also with the earthy succinates, except succinate of barytes. Hence barytes is the only earth precipitated from a neutral solution by succinate of ammonia. This salt likewise precipitates mercury and lead. It throws down iron from all solutions provided the iron be in the state of peroxide, and there be no excess of acid present.

I have shown that the atomic weight of succinic acid is 6.25, composition, and the agrees almost exactly with a previous experiment of Berzelius, who found succinate of lead a compound of

Succinic acid	•	•	6.26
Oxide of lead	•	•	14
			20.26

Berzelius subjected the acid to an analysis, and found its constituents

•	•	4.512
•	•	47.600
•	•	47.888
		100.000
	•	

This is equivalent to

2 atoms hydrogen	•	•	0.25
4 atoms carbon	•	•	3
3 atoms oxygen	•	•	3

6.25

Thus it appears that both the atomic weight and the atomic The same as constitution of succinic acid is precisely the same as that of

<sup>\*</sup> Morveau, Encyc. Method. Chim. i. 72.

<sup>†</sup> Wenzel's Verwandtschaft, p. 305.

<sup>§</sup> First Principles, ii. 137.

<sup>‡</sup> Pott.

<sup>||</sup> Annals of Philosophy, v. 99.

acetic acid. Yet no two acids can be more different in their properties. It is obvious that the difference between them can be explained only by a different arrangement in the atoms of each. If we were to admit that atoms are capable of uniting only two and two, forming primary compounds; that each of these may combine two and two, or one primary with a simple atom forming secondary compounds; and that each of these secondary compounds may combine two and two, or one secondary with one primary, or with one simple atom forming tertiary compounds, &c., it would be easy to see that compounds like succinic acid, which contain nine atoms, may have these atoms arranged in a great variety of ways, so that the primary and secondary compounds of which such compounds consist may be very different in the one body from what they are in the There is nothing, therefore, absurd or incongruous in conceiving, that two compounds possessed of very different properties may have the same atomic weights, and be even composed of the very same atoms. Berzelius views acetic acid as containing one atom of hydrogen more than succinic, and thinks this difference sufficient to explain the very different properties of the two acids. But I consider my experiments on perfectly pure and crystallized acetic acid, as proving decisively that its atomic weight is exactly 6.25. Nor are the characters of acetic acid such as would lead us to believe that it contains more hydrogen than succinic acid. It is as little liable to decomposition by heat, and yields less oil when distilled in combination with a base, than succinic acid.

Moroxylic

The moroxylic acid obtained by Klaproth, from a saline exudation on the bark of the Morus aiba,\* possesses the characters of succinic acid so exactly, that there seems no reason to hesitate about referring it to that acid. From the experiments of MM. Lecanu and Serbat, it appears that succinic acid exists also in the turpentines that exude from fir.†

Succinic acid being high priced is often adulterated, sometimes with tartaric acid, sometimes with bisulphate of potash, and sometimes with sal ammoniac. If we heat a little of the pure acid in a platinum or silver spoon, it is volatilized without residue; if it contains tartaric acid a quantity of charcoal will remain; if it contains bisulphate of potash a salt will remain; and sal ammoniac is detected by the ammoniacal smell emitted when the succinic acid is mixed with lime.

<sup>, \*</sup> Nicholson's Jour. vii. 129. † Ann. de Chim. et de Phys. xxi. 328.

### SECTION XIV. -- OF BENZOIC ACID.

Benzoin, or Benjamin, as it is sometimes called, is a kind History. of resin brought from the East Indies; obtained, according to Mr. Dryander, from the styrax benzoe, a tree which grows in the island of Sumatra. This substance consists partly of a peculiar acid, described as long ago as 1608 by Blaise de Vigenere, in his Treatise on fire and salt, under the name of flowers of benzoin, because it was obtained by sublimation; but it is now denominated benzoic acid.

The usual method of obtaining this acid is to put a quan- Preparation. tity of benzoin, coarsely powdered, into an earthen pot, to cover the mouth of the pot with a cone of thick paper, and then to apply a very moderate sand heat. The benzoic acid is sublimed, and attaches itself to the paper. This method was tedious and difficult; it being hardly possible to prevent the heat from scorching the benzoin, and volatilizing some empyreumatic oil, which soils and injures the acid sublimed. Neuman proposed moistening the benzoin with alcohol, and distilling it in a retort with a low heat. The acid comes over immediately after the alcohol, partly in crystals and partly of the consistence of butter.\* Geoffroy ascertained, in 1738, that this acid may be obtained by digesting benzoin in hot water. A portion is taken up, which is deposited in crystals as the water cools. Scheele published a different method in 1775; which being easier and more productive than any of the preceding, is now preferred. This process is as follows: + Upon four parts of unslacked lime pour twelve parts of water, and after the ebullition is over add 96 parts more of water; then put twelve parts of finely pounded benzoin into a tinned pan; pour upon it first about six parts of the above milk of lime, mix them well together, and thus successively add the rest of the mixture of lime and water. If it be poured in all at once, the benzoin, instead of mixing with it, will coagulate, and run together into a mass. This mixture ought to be boiled over a gentle fire for half an hour, with constant agitation; then take it from the fire, let it stand quiet for an hour, in order that it may settle; pour off the supernatent limpid liquor into a glass vessel. Upon the remainder in the pan pour 96 parts of pure water; boil them together for half an hour, then take it from the fire, and let it settle; add the supernatent liquor to the former; pour upon the residuum some more water, boil it as aforesaid, and repeat the same

<sup>\*</sup> Neuman's Chemistry, p. 294.

process once more. At last put all the residuums upon a filter, and pour hot water several times upon them. During this process, the calcareous earth combines with the acid of benzoin, and separates it from the resinous particles of this substance. A small quantity of the resin is dissolved by the lime-water, whence it acquires a yellow colour. All these clear yellow leys and decoctions are to be mixed together, and boiled down to twenty-four parts, which are then to be strained into another glass vessel. After they are grown cold, muriatic acid is to be added, with constant stirring, till there be no farther precipitation, or till the mass taste a little sourish. The benzoic acid, which was before held in solution by the lime, precipitates in the form of a fine powder.

This process of Scheele gives  $1\frac{1}{3}$  of benzoic acid from 10 parts of bezoin. The process of Stolze is still more productive. By means of it we may obtain 1.8 of acid from 10 of benzoin. But the expense of the process would in this country be too great. It is as follows: Dissolve one part of benzoin in three parts of alcohol; put it into a crucible and neutralize it exactly with carbonate of soda, dissolved in a mixture of eight parts water and three parts alcohol. Then add two parts more of water, and distil off the alcohol. Decant the aqueous liquid remaining in the retort from off the resin which will have precipitated, and wash this resin with pure water. Decompose the benzoate of soda contained in this liquid by sulphuric acid.\*

Mr. Hatchett has observed, that when benzoin is digested in sulphuric acid, a great quantity of beautifully crystallized benzoic acid is sublimed. This process is the simplest of all, and yields the acid in a state of purity; it claims, therefore, the attention of manufacturers.+

Properties.

Benzoic acid, thus obtained, is a fine light white elastic body in fine needles, which is not brittle, but has rather a kind of ductility. Its taste is sweet, hot, and somewhat bitter. Its odour is slight, but peculiar and aromatic.‡ Its specific gravity is 0.657.§ It hardly affects the infusion of violets, but it reddens that of turnsol, especially when kot.

Heat volatilizes this acid, and makes it give out a strong

- \* Berlinischer Jahrbuch der Pharmacie, xxv. 1, 75.
- † Hatchett's Additional Experiments on Tannin. Phil. Trans. 1805.
- ‡ This odour is owing to a small portion of aromatic oil which adheres to the acid. It has been obtained without any smell by Giese. See Phil. Mag. xiv. 331.
  - § Hassenfratz, Ann. de Chim. xxviii. 11.
  - Morveau, Encyc. Method. Chim. i. 44.

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odour, which excites coughing. When exposed to the heat of the blow-pipe in a silver spoon, it melts, becomes as fluid as water, and evaporates without taking fire. It only burns when in contact with flame, and then it leaves no residuum behind. When thrown upon burning coals, it rises in a white smoke. When allowed to cool after being melted, it hardens, and a radiated crust forms on its surface.\* When distilled in close vessels, the greater part of it sublimes unaltered, but some of it is decomposed. This portion is converted almost entirely into oil and carburetted hydrogen gas.

This acid is not altered by exposure to the air. Two hundred parts of cold water dissolve 1 part of it; + but 1 part of it dissolves in  $24\frac{1}{2}$  parts of boiling water. +

It combines with bases, and forms salts known by the name of benzoates. The alkaline benzoates are soluble in water. So are the benzoates of barytes, strontian, and magnesia. Those of alumina, yttria, and lime, are but sparingly soluble. The only metallic salts which form insoluble precipitates when mixed with benzoate of ammonia are those of tellurium, mercury, and peroxide of iron. Tellurium and mercury are precipitated white; iron orange. Berzelius has proposed benzoate of ammonia as an excellent agent for precipitating iron and separating it from other bodies with which it may be united. From the experiments of Hisinger the method appears to be a good one, provided the iron be in the state of peroxide and the liquid contain no excess of acid. I have been in the habit of using it in analyses or several years, and find it to answer the purpose perfectly.

Concentrated sulphuric acid dissolves benzoic acid without heat, or any other change, except becoming somewhat brown: when water is poured into the solution, the benzoic acid separates, and coagulates on the surface without any alteration. Nitric acid presents precisely the same phenomena, as does also the sulphurous acid. Neither the muriatic, nor the phosphoric acids, dissolve it. Acetic acid, when hot, dissolves it precisely as water does; but it crystallizes again when the acid cools.\*\*

Alcohol dissolves it copiously, and lets it fall on the addition of water.++ Boiling alcohol takes up its own weight.++ One

Lichtenstein.

<sup>†</sup> Bucholz, Gehlen's Journal fur die Chemie, Physik and Mineralogie, ix. 340.

<sup>#</sup> Bucholz, ibid.

<sup>§</sup> Afhandlingar, i. 171.

<sup>|</sup> Ibid. iii. 152.

<sup>¶</sup> Lichtenstein.

<sup>\*\*</sup> Ibid.

tt Ibid.

<sup>‡‡</sup> Wenzel's Verwandtschaft, p. 302.

hundred parts of cold absolute alcohol dissolve scarcely 56 parts of benzoic acid.\*

This acid is sometimes used as a medicine, but much less frequently than formerly.

Composition.

I have shown by experiments, which I consider as decisive, that the atomic weight of benzoic acid is 15.+ Berzelius subjected it to analysis, and obtained

Hydrogen	•	•	• `	5.16
Carbon	•	•		74.41
Oxygen	•	• •	•	20.43
				· 100. ‡
These proportions corresp	ond w	rith		
6 atoms hydro	gen	•		0.75
15 atoms carbon	n	•	•	11.25
3 atoms oxyge	'n	•	•	3.00
				15.

And as these atoms give the true atomic weight of the acid, there can be no doubt that they represent its constituents; though in what way these atoms are arranged we have no accurate conception.

Sebacic acid.

Chemists had long suspected that an acid could be obtained from tallow, on account of the acrid nature of the fumes which it emits at a high temperature; but it was M. Grutzmacher who first treated of it particularly, in a dissertation *De Ossium Medulla*, published in 1748.§ Mr. Rhades mentioned it in 1753; Segner published a dissertation on it in 1754; and Crell examined its properties very fully in two dissertations published in the Philosophical Transactions for 1780 and 1782. It was called at first acid of fat, and afterwards sebacic acid.

But at the period when these chemists made their experiments, the characteristic properties of the different acids were not sufficiently known to enable them to distinguish acids from each other with precision. Thenard examined the subject in 1801, tried all the processes of Crell and Guyton Morveau, and found that the acids procured by them were either acetic or the acid employed in the process. Thenard found, however, that a peculiar acid was formed during the distillation of tallow. To it he consigned the appellation of sebacic acid. The experiments

<sup>\*</sup> Bucholz, Wenzel's Verwandtschaft, p. 302.

<sup>†</sup> First Principles, ii. 141. ‡ Annals of Philosophy, v. 181.

of this chemist were repeated in 1804 by Mr. Rose, who obtained similar results, and confirmed all the observations of the French philosopher.\* The subject soon after was resumed by Berzelius, who in an elaborate dissertation, published in 1806, proved that the sebacic acid of Thenard is nothing else than benzoic acid contaminated with some unknown substance derived from the fat, which alters some of its properties, but from which it may be freed by proper precautions.† There does not therefore exist, as far as we know at present, any acid to which the name of sebacic belongs.

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#### SECTION XV. -- OF CROCONIC ACID.

This acid was discovered by M. Leopold Gmelin while History. preparing potassium by Brunner's process, of which an account has been given in the first volume of this work (p. 396).

During the whole process of preparing potassium, by exposing charred cream of tartar to a strong heat in an iron bottle, there passes off a combustible gas, the nature of which has not been examined. It is accompanied with a cloudy-looking body, which gradually forms a gray-coloured deposite in the tube of the apparatus. There is much of this gray matter also in the black substance, which chokes up the iron tube of the apparatus, and also in what comes over into the copper receiver, but mixed with potassium and charcoal. This gray matter dissolves in a great measure in water, and the solution has a yellowish brown colour. If it be exposed to spontaneous evaporation, two distinct kinds of crystals make their appearance in it. The first consist of long needles of an orange colour, which consist of croconic; acid united to potash; the second kind of crystals consist of bicarbonate of potash, coloured yellow probably by a little croconic acid.

The acid was separated from the croconate of potash by digesting it (reduced to a fine powder) for some hours in absolute alcohol, holding in solution as much sulphuric acid as was just sufficient to saturate the potash contained in the salt. The sulphate of potash remained undissolved, while the croconic acid was taken up by the alcohol.

The light yellow alcoholic solution being evaporated on the Propertical water bath, left the croconic acid in the state of a fine lemon yellow opaque crust, consisting of very fine grains. It dissolves readily in water; the solution has a lemon yellow colour, and

<sup>\*</sup> Gehlen's Jour. iii. 170.

<sup>+</sup> Afhandligar, i. 170.

<sup>‡</sup> So called on account of its yellow colour from xeonos, crocus, saffron.

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when left to spontaneous evaporation, deposites small yellow-coloured grains and needles, which undergo no alteration when exposed to a heat of 212°. These crystals have no smell. They have a very acid and sharp taste as if they contained iron, and they strongly redden litmus paper. When heated they leave a charcoal which burns away without leaving any residue whatever.

Croconic acid when saturated with potash shoots out into the same needles of croconate of potash from which it was originally procured. Croconate of potash is precipitated light yellow by barytes water and muriate of barytes, and the precipitate dissolves readily in muriatic acid. When the solution is mixed with muriate of lime, and allowed to stand for 24 hours, small light yellow grains of croconate of lime are deposited which are soluble in water.

Sulphate of magnesia, alum, bimuriate of titanium, muriate of chromium, muriate of uranium, muriate of manganese, muriate of cobalt, muriate of nickel, and sulphate of zinc, when mixed with croconate of potash occasion no precipitate. Bimuriate of antimony and binitrate of bismuth occasion lemon yellow precipitates, redissolved by an addition of the acid salts. Protomuriate of tin throws down an orange yellow precipitate from croconate of potash. Acetate of lead throws down lemon yellow flocks, again dissolved by the addition of nitric acid. The solution of sulphate of iron is rendered brownish yellow when mixed with croconate of potash, and permuriate of iron by the same mixture becomes black or grayish-red if in very minute quantity.

Sulphate of copper forms with it a green solution, and after some hours deposites small orange crystals of croconate of copper. Nitrate of mercury behaves like acetate of lead, except that the precipitate is not so easily dissolved by nitric acid. With nitrate of silver croconate of potash forms an aurora red precipitate, which dissolves in nitric acid with the evolution of a little gas, and the solution is colourless.

Croconate of potash dissolves in nitric acid with effervescence. But the acid is not destroyed, it is only altered in its qualities; for on evaporation no saltpetre is obtained, but yellow crystals, differing in some respects from croconate of potash. Chlorine seems to act in the same way as nitric acid. But iodine does not seem capable of altering its properties.

The croconate of potash was subjected to analysis by Gmelin, and found a compound of

l atom croconic acid			•	7.875		Class I, Div. II.
1 atom potash			•	6		
2 atoms water		•	•	<b>Ž·2</b> 5		Compositio
TTT 1 1 1 2 2 1 2 2 4 4 4 4 4 4	1 her	h	ooting	16·125	ovido o	f
While his analysis of the acid	ı by	H	eating	it with	oxide o	L
copper gave						
Carbon .	,	•	•	23.80		
Oxygen .		•	•	25.54		
Hydrogen		•	•	0.15		
This corresponds nearly with						
1 atom hydrogen			•	0.125		
5 atoms carbon		•	•	3.75		
4 atoms oxygen		•	•	4		
	*			7.875		

So that according to this analysis the atomic weight of croconic acid is 7.875. I think it probable from Gmelin's experiments, that croconic acid contains no hydrogen, but is a compound of 5 atoms carbon and 4 of oxygen, and that its atomic weight is 7.75. I attempted to determine the atomic weight of this acid by double decomposition. But the experiment was upon too small a scale to be decisive. So far as it went it was favourable to the notion that the atomic weight is 7.75.\*

# SECTION XVI. -- OF GALLIC ACID.

There is an excrescence, known by the name of nutgall, History. which grows on some species of oaks. This substance contains a peculiar acid, called from that circumstance gallic acid; the properties of which were first examined with attention by the commissioners of the Academy of Dijon, and the result of their experiments was published in 1777, in the third volume of their Elements of Chemistry.† In these experiments, however, they employed the infusion of galls, in which the acid is combined with tannin. It was reserved for Scheele to obtain it nearly in a state of purity.

1. He observed in an infusion of galls made with cold water a sediment, which proved on examination to have a crystalline form and an acid taste. By letting an infusion of galls remain a long time exposed to the air, and removing now and then the mouldy skin which formed on its surface, a large quantity of

<sup>\*</sup> See Gmelin's paper in Poggendorf's Annalen, iv. 31.

<sup>†</sup> Vol. iii. p. 403.

Chap. I. this sediment was obtained; which being edulcorated with cold water, redissolved in hot water, filtrated and evaporated very slowly, yielded an acid salt in crystals as fine as sand.\*

Deyeux has proposed a much speedier method of obtaining gallic acid; + but it does not succeed without a good deal of precaution. It consists in exposing pounded nutgalls in a large glass retort to a heat cautiously and slowly raised. A number of brilliant white crystalline plates are sublimed, which possess all the properties of gallic acid. Care must be taken not to apply too great a heat, and to stop the process before any oil begins to come over, otherwise the crystals will be redissolved, and the whole labour lost.

M. Braconnot has contrived another process, which appears to be both more economical, and more effectual than either of the preceding ones. It is merely an improvement of the process of Scheele, and is as follows:

Two hundred and fifty grammes of nutgalls were infused for four days in a littre of water (nearly half a pound avoirdupois of nutgalls in a wine quart of water), taking care to agitate the mixture from time to time. The whole was then squeezed through a cloth, and the liquid passed through a filter. then left in an open glass decanter from July 22 to September 22, or two months. Its bulk had not sensibly diminished; but it had deposited a considerable quantity of crystals of gallic acid. These were separated by squeezing the liquid through a cloth. The liquid, when evaporated to the consistence of a syrup, deposited an additional quantity of crystals which were separated in the same manner. The residual matter of the nutgalls from which the infusion had been procured, when moistened with water and left to spontaneous fermentation, yielded an additional crop of crystals when treated with hot water. that nutgalls when properly treated may be made to yield the fifth part of their weight of gallic acid.

By these different processes M. Braconnot obtained 62 grammes of gallic acid, still coloured and mixed with an insoluble powder. It was boiled with 18 cubic inches of water, and filtered while boiling hot. The liquid on cooling deposited 40 grammes of crystals of gallic acid of a yellowish-white colour. The mother water was brown, and when properly evaporated

<sup>•</sup> Stockholm Trans. 1786.—The crystals obtained by this method always contain a portion of tannin, and are of a brown colour.

<sup>†</sup> This method was in fact discovered by Scheele; but Deyeux repeated it, and pointed out the proper precautions. See Crell's Annals, i. 29. Eng. Trans.

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yielded 10 grammes more of crystallized gallic acid, darker coloured than the first crystals. To free these crystals entirely from colouring matter, they were mixed with eight times their weight of water, and about the fifth of their weight of ivoryblack, and the mixture was kept for about a quarter of an hour at the boiling temperature. It was then filtered while hot; on cooling it concreted into a mass of perfectly white crystals of gallic acid, which were separated from the liquid by pressure in a cloth.\*

Gallic acid obtained by this last process is nearly pure, and it may be freed from the tannin which still adheres to it by sublimation.

When thus obtained it is snow white, and is in small crystals properties. having a foliated fracture. The shape of the crystals is usually a flat rectangular prism, or a flat rectangular plate like mica. Mr. Brooke describes it as a doubly oblique prism.† But it is evident from his own descriptions, that the sides M, M' of his figure are inclined to each other at right angles, so that the prism must be rectangular and not oblique.

The taste of sublimed gallic acid is bitter, and it leaves in the mouth an impression of sweetness. It does not redden paper stained blue with litmus. The acid obtained by Braconnot's process has a sour taste.

It is soluble in  $1\frac{1}{2}$  parts of boiling water, and in 12 parts of cold water. When this solution is heated, the acid undergoes a very speedy decomposition. Alcohol dissolves one-fourth of its weight of this acid at the temperature of the atmosphere. When boiling-hot, it dissolves a quantity equal to its own weight. It is soluble also in ether. The solutions are colourless.

Gallic acid in crystals is not altered by exposure to the air. Neither oxygen gas, the simple combustibles, nor azote, seem to have any particular action on it. When the solution of this acid in water is exposed to the air, it gradually acquires a brown colour, and the acid is destroyed; the surface of the liquid becoming covered with mouldiness.

It combines with alkaline bodies, separating the carbonic acid if they were in the state of carbonates. The compounds formed have received the name of gallates; but hitherto have scarcely been examined. Indeed they may be said not to exist. For bases, as has been shown by Mr. Sertürner, have the property of acting on gallic acid and speedily decomposing it.‡

<sup>\*</sup> Ann. de Chim. et de Phys. ix. 181. † Annals of Philosophy, vi. 119. † Schweigger's Journal, iv. 410.

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When nitric acid is poured on this acid, a brisk effervescence takes place, hert is evolved, and the acid is dissolved very rapidly. The solution has a red colour, and when concentrated, crystals of oxalic acid are deposited, and a white insoluble matter also appears.

To a solution of 13.19 grains of bicarbonate of potash (containing 6 grains of potash), I added 8 grains of crystallized and anhydrous gallic acid. There was a strong effervescence which accompanied the solution of the acid. But after the whole acid was dissolved the liquid still retained an alkaline taste, and rendered cudbear paper violet as alkalies do. Even the addition of 8 more grains of the acid did not destroy the alkaline nature of the liquid. The solution was at first colourless; but after two days it became green, and this colour gradually deepened so much, that the liquid became opaque and looked like When evaporated to dryness it left a substance like pitch, which dissolved with effervescence in nitric acid, and the solution was brown. It is obvious from this that the acid was decomposed by the action of the potash on it. Accordingly the solution of gallate of potash in water does not exhibit the characteristic properties of gallic acid, when mixed with a solution of sulphate of iron.

The characteristic property of gallic acid is to strike a deep blue with the salts of iron, particularly the sulphate. The tannin, which is another constituent of nutgalls, possesses the same property; but it has an exceedingly astringent taste, and throws down a buff coloured precipitate when dropt into an aqueous solution of glue. Tannin itself seems to possess acid qualities; but as it has never been obtained exempt from gallic acid, it is possible that it may owe these qualities to the presence of that substance.

Composition.

Berzelius subjected the gallate of lead to analysis, and found its constituents to be\*

Gallic acid	•	•	8.047	
Oxide of lead	•	•	14	
This gives us 8 for its ato	mic w	eight.	The acid itself, su	ıb-

jected to analysis, yielded

Hydrogen	•	•	•	5
Carbon	•	•	•	56.64
Oxygen	•	•	•	38.36

100.00

This corresponds with			
3 atoms hydrogen	•		0:375
6 atoms carbon	•	•	4.5
3 atoms oxygen	•	•	3 、

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These atomic proportions give 7.875 for the atomic weight of gallic acid. This is 0.125, or an atom of hydrogen less than what results from the analysis of gallate of lead. I am disposed to prefer this last analysis as likely to be most correct; to consider the atom of gallic acid to weigh 8, and its constituents to be

7.875

4 atoms hydrogen	•	•	0.5
6 atoms carbon			4.5
3 atoms oxygen	•	•	3
			8

Dobereiner informs us, that when 100 parts of gallic acid dissolved in ammonia are left in contact with oxygen gas, they absorb 38.09 parts of that gas, and are converted into *ulmin*. 100 parts of gallic acid, according to the above estimate, consist of

Hydrogen	•	•	6.25
Carbon	•	•	56.25
Oxygen	•	•	<b>37·5</b>
			<del></del>
•			100

Now 38.09 of oxygen, in order to form water, must combine with 4.76 of hydrogen. There will remain 1.69 of hydrogen. So that ulmin ought to be a compound of

Hydrogen	•	•	1.49
Carbon	•	•	56.25
Oxygen	•	•	37.5

This is very little more than an atom of hydrogen, so that ulmin would appear from Dobereiner's observation to be a compound of

1 atom hydrogen,

6 atoms carbon,

3 atoms oxygen.\*

<sup>\*</sup> Gilbert's Annalen, lxxiv. 410.

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Ellagic Acid.

History.

It may be proper to notice here a substance which Braconnot has distinguished by this very absurd name (the French
word galle inverted). It possesses imperfectly acid properties,
and was extracted from nutgalls at the same time with gallic
acid. It would appear from a note of Chevreul that it had been
already detected by him, and several of its properties described
in the article tannin, published in the chemical part of the Encyclopædie Methodique, in 1815. But he had not given it a name,
and does not seem to have been aware of its acid properties.\*

Ellagic acid was obtained by Braconnot by filtering the solution of gallic acid obtained from the crystals which had formed spontaneously in the infusion of nutgalls. A powder remained upon the filter, which was ellagic acid mixed with a certain quantity of gallate of lime. To free it from this salt it was treated with a dilute solution of potash, which dissolved the acid with the evolution of a considerable quantity of heat. The solution had an intense yellow colour, and gradually let fall a pretty considerable quantity of pearl-coloured powder, which was separated by the filter and decomposed by dilute muriatic acid.

Properties.

The ellagic acid thus obtained is a white powder with a slight shade of buff. It is tasteless, and is not sensibly soluble even in boiling water. It does not decompose the alkaline carbonates even when assisted by heat. But it unites with caustic soda and potash, and destroys their alkaline characters. These salts are insoluble in water. But they become soluble if a little potash or soda be previously dissolved in that liquid. The solution has a very deep buff colour. The ellagate of ammonia is likewise insoluble, and does not become soluble even when an excess of ammonia is added. When this acid is agitated in lime water it separates the lime from the liquid. Nitric acid does not seem to act upon it at first, but if we continue the digestion it gradually assumes a blood-red colour.

Ellagic acid does not combine with iodine. When heated it does not melt, but burns away with a sort of scintillation, without emitting flame. When distilled it leaves charcoal and produces a yellow vapour, which condenses into transparent crystals of a fine greenish-yellow colour. This sublimate is tasteless and insoluble in water, alcohol, and ether; but it dissolves readily in a solution of potash, and communicates a

yellow colour. So that these crystals possess the same characters as the acid powder itself.\*

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## SECTION XVII. -- OF ULMIC ACID.

The vegetable substance to which I gave the name of ulmin, History, was first noticed by Klaproth in 1804, who found it in a matter which had exuded from the bark of the elm. It was noticed by Berzelius in 1810, in his experiments on the bark of the pine, and on Jesuit's bark.† In the beginning of the year 1813 I published a set of experiments on this substance.‡ About the same time, a similar set of experiments leading to nearly the same conclusions was made by Mr. Smithson.§ In 1830, M. Polydor Boullay published a set of experiments on it, in which he showed that it possessed the properties of an acid, and therefore gave it the name of ulmic acid.

Ulmic acid appears to be a vegetable substance of very great importance. It not only exists ready formed in bark, but it makes its appearance in a great variety of vegetable decompositions. M. P. Boullay has found that when the sugar of grapes, dissolved in water, is heated with an alkaline ley, it is converted into ulmic acid. It constitutes the essential ingredient of peat and of umber. It would appear also to be an admirable manure, or rather to constitute what is usually called vegetable manure.

Ulmic acid when obtained from the exudation of the elm by Properties. dissolving the exudation in water, and precipitating the ulmic acid by an acid, which saturates the potash with which it was in combination, consists of dark brown flocks almost destitute of taste and smell. It dissolves in small quantity in water and alcohol. The solutions have a brown colour, but no taste. What is called moss-water is merely water in which this acid is dissolved. When heated, it swells and catches fire, but does not melt.

It combines with the different bases which it neutralizes, and forms compounds analogous to salts, and which therefore may be called *ulmates*. The solution of *ulmate of potash*¶ in water has a dark brown colour. Sulphate of iron precipitates it brown or sometimes green. All the acids throw down the ulmic acid by saturating the potash. Nitrate of silver throws it down of

<sup>\*</sup> Ann. de Chim. et de Phys. ix. p. 187.

<sup>+</sup> Afhandlingar, iii. 347.

<sup>‡</sup> Annals of Philosophy, i. 23.

<sup>§</sup> Phil. Trans. 1813, p. 64.

Ann. de Chim. et de Phys. xliii, 273.

<sup>¶</sup> This salt constitutes the usual exudation from the elm.

chap. I. a beautiful red. Nitrate of lead and sulphate of copper give precipitates approaching to black.

M. P. Boullay analyzed some of the ulmates, and found their

composition as follows:

1. Ulmat	e of s	ilver.	
Ulmic acid .	•	•	36.87
Oxide of silver	•	•	14.75
2. Ulmui	te of	lead.`	
Ulmic acid .		•	38.12
Oxide of lead .	•	•	14
3. Ulmate	of co	pper.	
Ulmic acid .	•	•	· <b>42·61</b>
Oxide of copper	•	•	5

These analyses give different numbers for the atomic weight of ulmic acid. Boullay considers the analysis of ulmate of copper as the most exact. According to it the atomic weight of ulmic acid is 42.61.

Composition.

He subjected ulmic acid itself to analysis, by heating it with oxide of copper, and obtained for the constituents

Hydroge	n	•	•	•	4.8
Carbon	•	•	•	•	<b>56·7</b>
Oxygen	•	•	•	•	38.5
					1000

These numbers are very nearly in the ratios of

1 atom hydrogen		•	0.125
2 atoms carbon	•	•	1.5
1 atom oxygen	•	•	1
			•

2.625

If we multiply these atoms by 16 we obtain

16 atoms hydrogen	•	•		2
32 atoms carbon	•	•	•	24
16 atoms oxygen	•	•	•	16

**42** 

This gives us 42 for the atomic weight of ulmic acid, a number which approaches sufficiently near the number derived from the analysis of ulmate of copper, to give some probability to its being not far from the truth.

The reader will observe that the ratios between the atoms of carbon, hydrogen, and oxygen, which constitute gallic acid, are the same as those of ulmic acid. They are both resolvable

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into 1 atom of water and 2 atoms of carbon. But the atoms in ulmic acid are 64, while those in gallic acid are only 12. Hence the atomic weight of ulmic acid is  $5\frac{1}{3}$  times greater than that of gallic acid.

Dobereiner announced that when gallate of ammonia is exposed to the air it is converted into ulmate of ammonia. But this is not likely, the acid becomes dark coloured, but I find that the atomic weight is scarcely altered.\*

# SECTION XVIII. OF CRAMERIC ACID.

The Crameria triandra is a plant which vegetates in Peru, History. the root of which is remarkable for its astringent properties, and is said to be employed by the natives of the country where it grows, as a medicine of great efficacy in cases of atonic hæmorrhages. It is said to be brought to London in great quantities for the purpose of giving the requisite colour to artificial imitations of wine. This root attracted the attention of M. Peschier, apothecary at Geneva, who detected in it a new acid, which he has distinguished by the name of crameric acid. He obtained this acid in the following manner:

The root (particularly the bark) was boiled with water, and by this means a strong decoction was obtained, which had an astringent taste, and struck a black with sulphate of iron. To free it from the tannin, which it was presumed to contain, the decoction from an ounce of the root was mixed with a solution of 48 grains of gelatine, which occasioned a reddish brown deposite weighing 126 grains. To deprive the decoction of its colouring matter and of its gallic acid, which it still contained, 200 grains of sulphate of iron were added for every ounce of the root employed in making the decoction, and the liquid is then diluted with 7 or 8 pounds of water, and filtered. By this means it is rendered nearly colourless. It is then boiled with a sufficient quantity of chalk to decompose all the sulphate of iron which it still retains, and to saturate the crameric acid The whole liquid is now passed through the present in it. filter and concentrated to the requisite degree. The lime is to be thrown down with carbonate of potash, and the cramerate of potash is precipitated by acctate of lead. The cramerate of lead being properly washed, is decomposed by a current of sulphuretted hydrogen gas. The liquid being filtered and evaporated to the requisite consistency, nothing remains but a solution of crameric acid in water.

<sup>\*</sup> See p. 103.

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Properties.

Crameric acid thus obtained has a strong acid taste, and leaves upon the tongue a peculiar styptic sensation. It cannot be made to crystallize. It has no action upon the salts of lime and magnesia, but it decomposes all the salts of barytes and strontian, forming two salts with each, a supersalt which is soluble, and a subsalt which is insoluble in water. Cramerate of barytes is not decomposed nor altered by sulphuric acid. So that crameric acid has a stronger affinity for barytes than sulphuric acid has. It throws down the salts of lead white. Cramerate of potash, soda, ammonia, lime, and barytes, throw down the salts of iron yellow. It has no sensible action on the other metalline salts.

Cramerate of potash crystallizes in six-sided prisms.

Cramerate of soda forms large crystals, having the same shape, and efflorescing when exposed to the air.

Cramerate of ammonia yields feather-shaped crystals.

All these salts are insoluble in alcohol. They have little taste, and when thrown into a salt of barytes they occasion a precipitate.

Such are the properties of crameric acid, pointed out by M. Peschier. They will require to be verified, and I suspect rectified in several points, before the peculiarity of this acid be fully demonstrated, and its characters accurately determined.\*

#### SECTION XIX. -- OF KINIC ACID.

History.

Mr. Deschamps, junior, an apothecary in Lyons, published a method of extracting from yellow Peruvian bark a peculiar salt, to which the physicians of Lyons ascribed the febrifuge properties of that bark. His process was very simple; the bark was macerated in cold water, and the infusion concentrated by evaporation. It was then set aside for some time in an open vessel. The crystals of the salt gradually formed and separated, and they were purified by repeated crystallizations. From 100 parts of the bark about 7 parts of these crystals were obtained.

This salt was examined by M. Vauquelin, who proved it to be composed of lime united to a peculiar acid, to which he gave the name *kinic*, borrowed from the term *quinquina*, applied by the French writers to the bark from which the salt was extracted.

Deschamps' salt then is *kinate of lime*. M. Vauquelin separated the lime from the kinic acid by means of oxalic acid.

<sup>\*</sup> See Jour. de Pharmacie, vi. 34. + Ann. de Chim. xlviii. 162.

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MM: Pelletier and Caventon obtained it from the alcoholic tincture of gray cinchona by distilling off the alcohol after having added a sixth part of its weight of water. The liquid remaining in the retort was freed from the fatty matter and the brown resin which had separated during the distillation, and was boiled for some time with a great excess of magnesia and then filtered. Being evaporated nearly to dryness, it assumed the appearance of a magma, which being digested in alcohol left a white salt consisting of kinate of magnesia. It was decomposed by lime, and the kinate of lime in its turn decomposed by means of oxalic acid, and the kinic acid was obtained in crystals by the requisite concentration.\*

Kinic acid thus obtained, when pure, has a strong acid taste Properties. without any bitterness. The crystals have a good deal of resemblance to those of tartaric acid. They are transparent and colourless, and destitute of smell. Their specific gravity is 1.637. They are soluble in alcohol. At the temperature of 48° they dissolve in  $2\frac{1}{2}$  times their weight of water. When boiled with starch dissolved in water, they convert it into sugar. Distilled with alcohol, they form an ether similar to the tartaric ether of Thenard. Nitric acid converts this acid to the oxalic. Sulphuric acid decomposes it, and gives it at first a fine green colour.†

It combines with bases, and forms a genus of salts called *kinates*. All these salts are soluble in water. Hence it happens that kinic acid is not capable of throwing down any of the bases when dropped into saline solutions. In this respect it resembles acetic acid.

Kinates of lime, barytes, and copper, were analyzed by MM. composition. Henry and Plisson, who found them composed as follows:

1. 1	Kinate	of lin	ie.
Kinic acid	•		22.869
Lime .	•	•	3.5
2. K	inate o	f barg	ytes.
Kinic acid		•	23.091
Barytes	• .		9.5
3. <i>I</i>	Xinate d	of cop	per.
Kinic acid	•	•	23.46
Oxide of c	opper	•	5

These numbers make it probable that the atomic weight of

<sup>\*</sup> Ann. de Chim. et de Phys. xv. 304.

<sup>+</sup> Henry and Plisson; Ann. de Chim. et de Phys. xli. 326.

chap. I. kinic acid is about 23. The same chemists subjected the acid to an analysis, and found the constituents to be

Hydrogen	•	•	•	5.560
Carbon .		•		34.115
Oxygen .	•	•	•	60.325

100.000\*

Now the smallest number of atoms that agrees with these proportions and with the atomic weight derived from the analysis of the salts is,

10 atoms hydrogen	•	•	1.25
10 atoms carbon	•	•	· <b>7·50</b>
15 atoms oxygen	•	•	15
			23.75

But this gives the atomic weight too high. If we abstract an atom of carbon, and consider the acid as composed of

10 atoms hydroge	n.	•	1.25
9 atoms carbon	•	•	6.75
15 atoms oxygen	-	•	15
			99

we obtain 23 for the atomic weight. This, therefore, is the constitution of this acid that agrees best with the analytical results of Henry and Plisson.

#### SECTION XX. -- OF PYROKINIC ACID.

History.

This acid was discovered by MM. Pelletier and Caventou about the year 1820. It is obtained by distilling kinic acid. When heat is applied to this acid in a retort it swells up, blackens, and gives out a white acrid smoke. There passes over into the receiver a brown, oily, and very acid liquid, while some crystals make their appearance in the neck of the retort. These crystals were redissolved, and the liquor filtered through moistened cotton to retain the oil. This liquid being slowly evaporated, yielded crystals of pyrokinic acid.

Properties.

Pyrokinic acid crystallizes in tufts composed of diverging needles. It is at first brown, but by repeated crystallizations becomes colourless. Its taste is acid, and it is destitute of smell. It is very soluble both in water and alcohol. It forms soluble salts with potash, soda, ammonia, barytes, and lime. It occasions a

<sup>\*</sup> Henry and Plisson; Ann. de Chim. et de Phys. xli. 327.

slight precipitate in acetate of lead and nitrate of silver. Its characteristic property is that it precipitates the persulphate of \_ iron of a beautiful green colour. So delicate a test is it of iron, that it assumes a green colour when combined with lime or barytes, containing traces of that metal. It is neither affected by solutions of glue nor of tartar emetic.\*

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## SECTION XXI. -- OF MECONIC ACID.

This acid exists in opium, probably in combination with History. morphine. It was discovered by M. Sertürner, and called by him meconic acid, from the Greek word μηχων, a poppy. Various modes of extracting this acid from the infusion of opium have been proposed; but none of them seems to be very good. The following process, which was contrived by Robiquet, yields meconic acid, but we do not succeed by it in obtaining the whole of that acid which exists in the liquid.

Boil the infusion of opium with rather a greater quantity of magnesia than is sufficient to precipitate the whole of the morphine. Digest the precipitate in alcohol till the whole of the morphine is dissolved. There remains behind a quantity of magnesia united with meconic acid. Sulphuric acid dissolves this matter, and forms with it a brown coloured solution. Muriate of barytes being dropt into the solution a precipitate falls, consisting of sulphate of barytes, and meconate of barytes slightly tinged red. Weak sulphuric acid being long digested upon this precipitate, decomposes the meconate; the meconic acid dissolves in the water, while the sulphate of barytes remains behind. The water being evaporated, allows the meconic acid to deposite in the form of brown crystals. In this state it is contaminated with a colouring matter which renders it much less soluble in water than when pure, and causes the meconate of magnesia and of barytes to precipitate; for when these salts are pure, they are soluble in water. These brown crystals are to be dried at a low temperature, and then to be exposed to a higher temperature, but one not sufficiently high to decompose the colouring matter. The meconic acid sublimes, and is deposited on the upper part of the retort.

A still easier process for procuring this acid has been recommended by Dr. Hare. Drop acetate of lead into the aqueous infusion of opium; meconate of lead precipitates: wash this precipitate, mix it with water, and pass a current of sulphuretted

<sup>\*</sup> Ann. de Chim. et de Phys. xv. 341.

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hydrogen through it. The lead is separated, and the meconic acid dissolves in the water. Filter the solution, and evaporate till the meconic acid falls in crystals.

Properties.

Meconic acid thus obtained is white, and is usually crystallized in long needles, or square plates, though sometimes it affects other forms. It melts when heated to the temperature of about 250°, and as soon as melted, it begins to sublime without any decomposition.

It is exceedingly soluble, both in water and alcohol. Its taste is acid, and it reddens vegetable blues. It combines with the different bases, and forms salts, distinguished by the name of meconates. The meconates of potash, soda, and ammonia, are soluble in water. This is the case also with the meconates of barytes, lime, and magnesia.

When meconic acid is dropt into solutions of the peroxide of iron, it strikes a strong red colour, similar to the change produced upon the same saline solutions by the sulpho-cyanic acid. But it does not occasion any precipitation in these liquids. When dropt into a solution of sulphate of copper, the colour of the liquid changes to a fine emerald green. No precipitate falls at first; but a pale yellow powder is at last deposited. This acid likewise produces slowly a precipitate in the solution of corrosive sublimate.\*

#### SECTION XXII. OF BOLETIC ACID.

History.

This acid was discovered in 1811, by M. H. Braconnot, while examining the expressed juice of the boletus pseudo-igniarius.+ He obtained it by the following process: The juice of the boletus was evaporated to a thick syrup by a very low heat. The residual matter was digested in alcohol. The portion left undissolved by the alcohol was dissolved in water, and nitrate of lead dropped into the solution. A white precipitate fell, which being edulcorated was mixed with water, and decomposed by a current of sulphuretted hydrogen gas. The liquid being filtered and evaporated exhibited two distinct acids. The one, which existed only in small quantity, was phosphoric acid, and deliquesced when exposed to the air. The other constituted permanent crystals. It was boletic acid. To obtain it in a state of purity it was dissolved in alcohol, and crystallized by evaporating the solution. In this state it possesses the following properties:

<sup>•</sup> Robiquet, Ann. de Chim. et de Phys. v. 282.

<sup>†</sup> Ann. de Chim. lxxx. 272.

Its colour is white, it is not altered by exposure to the air, Class I. and consists of irregular four-sided prisms. Its taste is similar to that of tartar. It requires 180 times its weight of water to Properties. dissolve it at the temperature of 68°. It is soluble in 45 times its weight of alcohol.

The aqueous solution reddens vegetable blues. Nitrate of lead occasions a precipitate in it which is redissolved by agita-It precipitates the red oxide of iron from its solutions completely in the form of rust-coloured flocks; but it does not throw down the black oxide of this metal. It precipitates nitrate of silver in the state of a white powder which is soluble in nitric Nitrate of mercury is precipitated in the same state; but the precipitate dissolves with difficulty in nitric acid. Neither lime water nor barytes water produces any effect upon the aqueous solution of this acid. When heated it rises in white vapours, which irritate the throat, and condense on surrounding bodies in the form of a farinaceous powder. distilled the greatest part sublimes unaltered, excepting that it afterwards crystallizes more regularly. At the same time a little tiquid appears having a strong smell of acetic acid.

Boletate of ammonia is a salt which crystallizes in flat four- salts. sided prisms, and is soluble in 26 times its weight of water at 68°. Its taste is cooling, saline, and somewhat sharp. When heated it melts, swells, and sublimes. It precipitates red oxide of iron; but does not alter sulphates of lime, alumina, or manganese. It slowly precipitates nitrate of copper in blue silky needles.

Boletate of potash is very soluble in water, and crystallizes with difficulty. Acids precipitate the boletic acid from it.

When boletic acid is heated with carbonate of lime it dissolves it with effervescence. The boletate of lime crystallizes in flat four-sided prisms. This salt has little taste, and requires at least 110 times its weight of water at the temperature of  $72\frac{1}{2}$ ° to dissolve it. It is decomposed by oxalic and sulphuric acids.

Boletate of barytes is an acidulous salt in white plates little soluble in water or nitric acid. When thrown on a red-hot iron it burns rapidly with a red flame and striking scintillations, leaving for residue carbonate of barytes.

When this acid is heated with iron filings and water, hydrogen gas is emitted, and a yellow liquor is obtained with an inky taste.

Such are the properties of boletic acid as they have been ascertained by Braconnot. Hitherto no other chemist has repeated his experiments.

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SECTION XXIII. --- OF CAMPHORIC ACID.

History.

Camphor is a well-known white crystalline substance, of a strong taste and smell, obtained from a species of laurel in the East Indies. It is so volatile that it is not readily melted in open vessels, and so inflammable that it burns even on the surface of water.

When camphor is set on fire in contact with oxygen gas, it burns with a very brilliant flame; much caloric is disengaged, water is formed, the inner surface of the vessel is covered with a black matter, which is undoubtedly charcoal, and a quantity of carbonic acid gas is also produced.\* Hence it follows, that it is composed of hydrogen and carbon, at least principally.

Mr. Kosegarten, by distilling nitric acid off camphor eight times successively, obtained an acid in crystals,† to which the name of *camphoric acid* has been given.

His experiments have been repeated by Mr. Bouillon Lagrange. The process for obtaining camphoric acid, as described by this chemist, is as follows: Put into a retort I part of camphor and 8 parts of nitric acid, of the specific gravity 1.33. Distil with a sand heat. A great deal of nitrous gas and carbonic acid gas is emitted, and a little camphor sublimes. This process must be repeated three times on the same camphor; so that 24 parts in all of nitric acid are necessary. After the third distillation, when the retort is allowed to cool, a number of crystals make their appearance in it. These are camphoric acid. They amount to somewhat less than the half of the camphor employed.

The experiments of Kosegarten and Bouillon Lagrange were confirmed in 1810, by Bucholz, who employed the following process for converting camphor into camphoric acid. Two ounces of camphor are put into a retort with  $1\frac{1}{2}$  lb. of nitric acid of the specific gravity 1.250, and half a pound of fuming nitric acid of the specific gravity 1.550. A moderate heat is applied, and about one-half of the acid is distilled off. This process is repeated three times, pouring back the acid which has distilled over each time. After the third distillation the camphoric acid is observed swimming on the acid in the retort like a butyraceous mass, after the whole has become cold. It is separated from the nitric acid by means of a glass funnel. When washed and dried it is camphoric acid in a state of purity.

<sup>\*</sup> Bouillon La Grange, Ann. de Chim. xxiii. 153.

<sup>†</sup> Kosegarten, de Camphora, &c. 1785.

In the year 1823 an elaborate set of experiments on camphoric acid and its salts was published by Dr. Rudolph Brandes.\* His process for preparing it was the same as that of Bucholz. He gives us the weight of nitric acid requisite to convert four ounces of camphor into camphoric acid; but as he has neglected to give us the specific gravity of the acid employed, his statements convey little information to the practical chemist.

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Camphoric acid thus prepared is in feather-shaped crystals. Properties. It has a white colour. Its taste is slightly acid and bitterish, and, according to Brandes, conveys an impression of camphor. At the common temperature of the air it has scarcely any smell, but when heated to 100° it gives out a perceptible odour of camphor. At the temperature of 100° it begins to give out a thick white vapour, having an acid and fatty smell: at 155° it melts into a transparent colourless liquid. When the temperature is still farther raised, it catches fire and burns with a clear flame, leaving scarcely any residue. If it be put into a heated porcelain tube, and oxygen gas be passed through it, the acid does not undergo any change, but is sublimed. If mere distillation it first melts, and then sublimes unaltered.

The following table shows the solubility of this acid in water of different temperatures, as determined by Dr. Brandes.

							amphoric acid.
$\mathbf{At}$	$54rac{1}{2}^{\circ}$	Fahr	enheit,	100	water	dissolve	1.13
	77	•	•	100	•	•	1.457
	99.5		•	100	•	• .	1.626
	122	•	•	100		•	2.459
	144.5	•	•	100	•	•	4.290
	180.5	•	•	100	•	•	5.29
	194	•	•	100	•	•	10.13
	$205\frac{1}{4}$	•	•	100		•	12.00

The following table, by the same chemist, shows the solubility of this acid in alcohol at different temperatures. Unfortunately he has neglected to specify the specific gravity of the alcohol employed.

			•		Camphoric acid.		
At 47°.75	•	•	100	alcohol	dissolve	106	
<b>64 ·5</b>		•	100	•	•	111	
77	•	•	100	•	•	115	
99 <b>·5</b>	•	•	100	•	•	161	
144 .5	•	•	100	•	•	121	

<sup>\*</sup> Schweigger's Jahrbuch, viii. 269.

<sup>†</sup> Bucholz, Gehlen's Jour. für die Chemie, Physick, und Mineralogie, ix. 339.

We see from this that alcohol at the temperature of about 100°, dissolves more of this acid than at higher or lower temperatures.

Oil of turpentine dissolves camphoric acid by the assistance of heat, and allows it to be deposited in crystals when the solution cools.

To determine the atomic weight of camphoric acid, Brandes analyzed several camphorates. The following table exhibits the results which he obtained.

1. Campho	rate of $\gamma$	ootas	h.
Camphoric acid	. •		12.46
Potash .	•	•	6
2. Camphe	orate of	soda	ı. <b>.</b>
Camphoric acid		•	12.6
Soda .	•	•	4
3. Camph	orate of	<sup>c</sup> lime	2.
Camphoric acid		•	13.44
Lime .	•	•	3.5
4. Camphor	rate of l	baryt	es.
Camphoric acid			12.76
Barytes .	•	•	9.5
5. Camph	orate of	lead	<b>!.</b>
Camphoric acid	•	•	12.12
Oxide of lead	•		14

The numbers after camphoric acid in this table indicate the atomic weight of the acid deduced from the respective analyses. They do not quite agree with each other. But if we leave out the camphorate of lime, which deviates too far, and take the mean of the four other analyses, we obtain very nearly 12.5 for the atomic weight of this acid.

Composition.

Brandes subjected the acid itself to an analysis by means of oxide of copper, and obtained for the constituents,

$\mathbf{H}\mathbf{y}\mathbf{d}\mathbf{r}\mathbf{o}\mathbf{g}\mathbf{e}\mathbf{n}$	•	•	5.618
Carbon	•	•	61.341
Oxygen	•	•	33.041

100.000

These numbers would give us for the atomic constitution of the acid,

6	atoms	hydrogen	•	•	0.75
		carbon	•	•	8.25
$4\frac{1}{2}$	atoms	oxygen	•	•	4.5

The atomic weight derived from these proportions is 13.5, which comes very near the atomic weight of the acid deduced \_ from the analysis of camphorate of lime.

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It is obvious that new experiments are still requisite before we can consider the atomic weight or atomic constitution of this acid as accurately determined.

# SECTION XXIV. OF SUBERIC ACID.

Cork, a substance too well known to require any description, History. is the bark of a tree which bears the same name. By means of nitric acid Brugnatelli converted it into an acid,\* which has been called suberic acid, from suber, the Latin name of the cork tree. Several chemists affirmed that this acid was the oxalic, because it possesses several properties in common with it. These assertions induced Bouillon Lagrange to undertake a set of experiments on suberic acid. These experiments, which have been published in the 23d volume of the Annales de Chimie, completely establish the peculiar nature of suberic acid, by showing that it possesses properties different from those of any other acid. Chevreul afterwards published a new set of experiments on it, which both serve still further to establish its peculiar nature, and make us better acquainted with its properties.†

Chevreul obtained this acid by digesting 1 part of cork in 6 parts of acid. After the acid had ceased to act, the whole was evaporated to the consistence of an extract, hot water was poured over it, and the mixture was digested for some time in a sand heat. When set aside, a matter like wax formed on the surface, and white tasteless flocks precipitated to the bottom. These substances were separated, and the liquid concentrated by evaporation. Suberic acid precipitated in powder, and towards the end of the process crystals of oxalic acid formed. I observed the formation of oxalic acid many years ago, while treating cork with nitric acid. But the most elaborate set of experiments on this acid was published by Dr. Rudolf Brandes during the years 1821 and 1822.‡ He not only examined the properties of the acid in detail, but determined the composition and properties of the different suberates.

Pure suberic acid has a white colour, and is not altered by Properties. exposure to the air. Its taste is acid, but not in the least bitter, unless when it is impure. It has no smell. When dried it

<sup>\*</sup> Crell's Annals, 1787, i. 154. + Nicholson's Journal, xxiii. 149.

<sup>‡</sup> Schweigger's Jahrbuch, ii. 393, iii. 83, and vi. 263.

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has no lustre. The crystals of it are imperfect needles. When heated it melts into a transparent liquid, which on cooling assumes a yellowish tinge. It melts at the temperature of 130°, and remains liquid till it be cooled down to 125°½ when it again congeals. The solid matter is fibrous and obviously crystallized on the surface. It requires a great deal of cold water to dissolve it, but it is very soluble in boiling water. The following table shows the solubility at different temperatures as determined by Brandes.

					•			Water.
At	48°	Fahr	enheit	1 part	of aci	id diss	olves	in 100·1
	$53\frac{1}{2}$	•	•	]	•	•	•	91.25
	183	•	•	1	•	•	•	5
	212	•	•	1	•	•	•	1.87

The following table shows the solubility of the acid in absolute alcohol according to the determination of the same experimenter.

 $100\,parts\,of\,boiling\,sulphuric\,ether\,dissolved 16\cdot 6\,parts\,of\,this\,acid.$ 

Suberic acid.

								puberro moras
At	<b>68°</b>	•		100 et	ther di	issolve	•	12.9
	<b>50</b>	•	•	100	•	•		12.82
	39		_	100	_	_	_	9.8

It is soluble also in volatile oils, particularly in oil of turpentine. When heated in a retort it is volatilized, and condenses on the upper part in long needles. It does not precipitate lime, barytes, or strontian water, nor the salts containing these alkaline earths. The alkalies dissolve it very well, and form with it neutral salts. It precipitates nitrate of silver, muriate of tin, sulphate of iron, nitrate and acetate of lead, and nitrate of mercury, but it does not precipitate sulphate of copper or sulphate of zinc.

Nitric acid has no action on it. It does not alter the colour of sulphate of indigo, provided it is free from yellow bitter matter.\*

Dr. Brandes, in order to determine the atomic weight of this acid, analyzed several of the *suberates*. The following table exhibits the results which he obtained.

# 1. Suberate of soda.

Suberic acid		•	•	12.55
Soda	•	•	•	4

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2. Subero	ite of	lime.	
Suberic acid	•	•	1 <b>k</b> 95
Lime .	•	•	3.5
3. Suberate	e of be	arytes.	•
Suberic acid	•	•	12.76
Barytes .	•	•	9.5
4. Suberate	of st	rontia	п.
Suberic acid	•		12.38
Strontian .	•	•	6.5
5. Suberate	of me	agnesi	$a_{ullet}$
Suberic acid	•	•	11.76
Magnesia .	•	•	$2 \cdot 5$
6. Subera	te of	silver.	
Suberic acid		•	12.29
Oxide of silver	•	•	14.75
7. Suberat	e of c	opper.	•
Suberic acid	•	•	11.93
Oxide of copper	•	•	5
8. Subera	ite of	lead.	
Suberic acid		•	12.56
Oxide of lead	•	•	14

The numbers after suberic acid denote its atomic weight according to each analysis. The experiments were made on a very small scale, which accounts in some measure for the want of accordance among them. The mean of the whole eight analyses gives us 12·15 for the atomic weight of suberic acid. And if we leave out the suberate of magnesia, which gives thelowest number, and which is not so easily analyzed as the others, we obtain for the atomic weight of this acid 12·21. So that the probable number from these analyses is 12·25.

Dr. Brandes analyzed 1.25 grain of suberic acid by means Composition. of oxide of copper, and obtained for the constituents,

Hydrogen	•	•	15.9856
Carbon	•	• •	37.2536
Oxygen	•	•	46.7608
			100 0000

100.0000

The number of atoms of each constituent, which correspond best with these proportions, is as follows,

16 atoms hydrogen	•	•	<b>2</b>
6 atoms carbon	•	•	4.5
6 atoms oxygen	. •	•	6

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This gives 12.5 for the atomic weight of suberic acid, very nearly the same as that deduced from the analysis of suberate of soda, which was made upon the greatest scale, and suberate of lead which furnishes the salt of easiest analysis. I am disposed therefore to consider 12.5 as the true atomic weight of this acid. Suberic acid is remarkable for the great proportion of hydrogen which it contains, a singular circumstance if we consider the great quantity of nitric acid employed in its formation.

#### SECTION XXV. -- OF PECTIC ACID.

History.

It has been long known that the juice of currants, gooseberries, cherries, apples, and many other fruits, when left exposed to the air, gradually assumes the form of a jelly. Some observations on this jelly had been made many years ago by Vauquelin;\* but it was M. Braconnot who first pointed out its acid nature, showed the method of procuring it pure, and described its characters in detail.† Some additional facts were afterwards brought to light by the experiments of Vauquelin.‡ Braconnot gave it the name of pectics acid, from the great tendency which it has to form a jelly with water.

It may be obtained from the roots of carrots, turnips, parsenips, &c., from the inner bark of most trees, from the greater number of fruits, so that it appears to be very universally scattered over the vegetable kingdom. One of the substances from which it is most easily procured is the common carrot. The method of proceeding is as follows: Having well washed the carrots, reduce them to a pulp by means of a grater. Express the juice and wash the dry residue with pure water, till it ceases when squeezed out of the pulp to be in the least Mix 50 parts of this washed and expressed pulp with 300 parts of water and one part of caustic potash. this mixture and boil it for a quarter of an hour. liquid through a cloth, and wash the undissolved portion with pure water. Mix all these liquids together, and add to them while still hot a very dilute solution of muriate of lime. pectate of lime formed immediately gelatinizes. It is collected and well washed upon a cloth. Then boil it for some minutes with water acidulated with muriatic acid, which dissolves the lime and the starch should any be present. The whole being now thrown on a filter it is in the state of a jelly, which may be washed with facility.

<sup>\*</sup> Ann. de Chim. v. 92. vi. 275.

<sup>†</sup> Ann. de Chim. et de Phys. xxviii. 173. xxx. 96. ‡ Ibid. xli. 46.

<sup>§</sup> From mnxlis, coagulum.

Vauquelin informs us that the process is facilitated by sub-soda, in the proportion of 5 parts for every 100 parts of the expressed pulp. The rest of his process is the same as that of Braconnot just described.

Thus obtained pectic acid has the form of a transparent and Properties. colourless jelly. Its taste is perceptibly acid, and it reddens paper stained blue by litmus. It is scarcely soluble in cold Boiling water dissolves it in small quantity. filtered solution is colourless, and does not let any sediment fall on cooling, and scarcely reddens litmus paper. It is coagulated into a jelly colourless like glass, by alcohol and all metallic solutions without exception; by lime and barytes water, by acids, by muriate and sulphate of soda, nitrate of potash, &c. Even sugar when added to the water, causes the pectic acid to assume the form of a jelly.

When dried upon a capsule it assumes the form of transparent plates, which do not adhere to the glass vessel. this state it scarcely swells when put into cold water; but it dissolves a little in boiling water, and the solution coagulates by all the different reagents as at first. When distilled in a retort, it yields a good deal of empyreumatic oil; but no ammonia nor muriatic acid, and leaves behind it a bulky coal. When mixed with water it has the property of disengaging carbonic acid from the alkaline carbonates.

When mixed with an excess of caustic potash in a platinum crucible, and gently heated, agitating the mixture carefully, it soon melts and assumes a brown colour. If we evaporate the liquid without increasing the heat much, we will observe that when the water is driven off what remains in the crucible again assumes a white colour, and if we examine it we shall find it to consist of oxalate of potash. By this process the pectic acid has been converted into oxalic acid.\*

With potash, pectic acid forms a salt which has little taste, salts. and is very soluble in water. Weak alcohol throws it down in the form of a jelly. When this jelly is dried it assumes a form resembling gum arabic, and scarcely adheres to the glass in which the evaporation was carried on. When heated it swells, and leaves a brown matter, which is ulmine united to potash. Pectate of potash, when in solution in water, is coagulated by all the substances which produce the same effect on pectic acid.

<sup>\*</sup> Vauquelin; Ann. de Chim. et de Phys. xli. 55.

The earthy and metallic salts decompose it by double affinity.

According to the analysis of Braconnot it is a compound of

Hence it would appear that its atomic weight is about 33.

Most of the other pectates are insoluble, and may be obtained by double decomposition.

Cold sulphuric acid has little action on it; when heat is applied sulphurous acid is given off and ulmine formed. When nitric acid is distilled off it, the residue furnishes oxalic acid.

Braconnot, in consequence of the property which this acid has of converting a vast quantity of water into a jelly, has proposed the introduction of it under that form as a very palatable food. The method of preparing these jellies is as follows: Boil a little pectic acid in the quantity of water which is to be converted into a jelly, then dissolve in the water a sufficient quantity of sugar previously seasoned by being rubbed over the skin of an orange, or by any other wished for seasoning, or add to the water a little alcohol previously properly seasoned. In either case the whole assumes the form of a jelly, the flavour of which will of course depend upon the nature of the seasoning employed.

These jellies liquefy with extreme facility when a little ammonia is poured upon them.

Braconnot is of opinion that the soluble pectates constitute a complete antidote against all metallic poisons, such as those of lead, copper, zinc, antimony, and mercury. His reason is, that the salts of all these metals are decomposed by pectate of potash, and the metalline pectate formed is quite insoluble, and therefore not likely to prove injurious to the animal economy. Though this inference is not quite unobjectionable, yet the insolubility of such pectates would form a reason for administering pectate of potash in all cases when a poisonous metallic salt had been taken into the stomach. Braconnot excepts corrosive sublimate, nitrate of silver, and tartar emetic, because the insoluble pectates obtained from them are soluble in an excess of pectate of potash.

Upon the whole, the properties of pectic acid are interesting, and its nature and properties deserve a much more complete, investigation than they have hitherto met with.

SECTION XXVI. -- OF STEARIC ACID.

Class I. Div. II.

Chevreul about the year 1813. He at that time gave to the Institute an account of an acid substance which enters into the composition of seaps, and to which he gave the name of margarine. In 1816 he distinguished it by the name of margaric acid. About the same time he found that margaric acid extracted from different bodies existed in two different states, and as the one contained more oxygen than the other, he distinguished them at first by the name of margarous and margaric acids. But he thought it afterwards better to give to margarous acid the name of stearic\* acid, and to retain the term margaric acid, which had been applied to the other at first.

The method of procuring stearic acid is as follows: Make a soap by boiling mutton suet and caustic potash together, with a sufficient quantity of water, till the whole is converted into soap. Dissolve one part of this soap in 6 parts of warm water, and mix the solution with about 40 parts of cold water, and leave it for some time in a temperature about 60° or between 60° and 70°. A substance precipitates having a pearly lustre, which is a mixture of bistearate of potash and margarate of potash. Collect this substance on the filter and wash it. liquid that has passed through the filter being mixed with a little acid to saturate the potash which it now contains in excess, will yield an additional quantity of this twofold soapy salt. repeating this process several times all the bistearate of potash and margarate of potash is obtained, and the water retains only the oleate of potash. The bistearate and margarate of potash is to be dried and dissolved in about 20 times its weight of hot When the alcohol cools a quantity of bisteaalcohol of 0.82. rate of potash mixed with margarate of potash precipitates, and oleate of potash and margarate of potash remains in solution in the alcohol.

The precipitated bistearate of potash and margarate of potash is to be again dissolved in boiling alcohol, which is to be set by to cool. The bistearate which now precipitates is much freer from margarate, and by repeating the solution in boiling alcohol two or three times, it is at last got perfectly pure. To determine whether the bistearate is quite pure, take a little of it and decompose it by muriatic acid. Put the acid which separates (after washing it) in water, the temperature of which is to be gradually raised. If the acid does not melt till the temperature of the water reaches 158° it is pure stearic acid. If

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it melts at a lower temperature it contains a mixture of margaric acid. The stearate of potash being thus obtained in a state of purity, it is decomposed by boiling it with muriatic acid and water. The stearic acid is to be separated when the mixture gets cold, and it may be freed from all admixture of muriatic acid by fusing it repeatedly in pure water.

Properties.

Stearic acid has a fine white colour, and when the fused acid is allowed to cool below 158° it crystaltizes in fine brilliant needles. It is tasteless and destitute of smell. It is insoluble in water. While liquid it may be mixed with hot alcohol in all proportions. If we heat I part of alcohol of the specific gravity 0.794 with one part of stearic acid to the temperature of 167°, we obtain a solution which remains liquid till cooled to 122°. It then crystallizes in brilliant scales, and it becomes quite solid at 113°. When stearic acid isheated with its own weight of ether of the specific gravity 0.727 in a tube shut by the finger, a solution takes place, which is limpid at 160°, but at 134° it becomes solid, and consists of a congeries of brilliant plates.

This acid combines with concentrated sulphuric acid without undergoing decomposition. It has the property of reddening vegetable blues. It combines with the bases and forms a class of salts called *stearates*. At the temperature of 212° it disengages carbonic acid from the carbonates of potash and soda.

When this acid is distilled it gives out a little carbonic acid and a little carburetted hydrogen, and an oily matter passes over which is stearic acid a little altered in its properties. When stearic acid is heated sufficiently in an open vessel it burns like wax. When digested with nitric acid it is converted into an acid which possesses peculiar properties, but which hitherto has been very little examined.\*

From the analyses of different species of stearates by Chevreul, it appears that the atomic weight is very nearly 33.33. The acid in its usual state is a hydrate, being composed of

It is obviously therefore a compound of

cThe small surplus of water is doubtless mechanically lodged between the particles of the acid.

<sup>\*</sup> See Braconnot; Ann. de Chim. xciii. 254; and Chevreul sur les corps gros, p. 28.

This acid was analyzed by Chevreul by means of oxide of Class L Div. II.

Copper, and he found the constituents to be Composition.

100.000

Oxygen . . . 7.377 Carbon . . . 80.145 Hydrogen . . . 12.478

.78

Now the number of atoms corresponding to these weights and to the atomic weight of the acid is the following:

2 atoms oxygen . . . 2
36 atoms carbon . . . 27
34 atoms hydrogen . . . 4.25
33.25

The analysis of Chevreul gives  $2\frac{1}{2}$  atoms oxygen instead of 2 atoms. But this would make the atomic weight too high. We see that stearic acid must be of a very complicated nature indeed, since it contains no fewer than 72 atoms.\*

### SECTION XXVII. -- OF MARGARIC ACID.

This acid was one of the first which Chevreul discovered, History. but it was only by degrees that he was able to distinguish between stearic and margaric acid. It may be obtained by the following process:

Soap made of olive oil and potash is to be macerated for 24 hours in twice its weight of cold alcohol. The oleate of potash is dissolved and the margarate of potash remains undissolved. It must be well washed with cold alcohol and then dissolved in 200 times its weight of boiling alcohol. When the liquid cools the margarate of potash shoots into crystals, but still contaminated with a little oleate of potash. Dissolve it again in hot alcohol and allow it to crystallize a second time. To see whether it be now pure margarate of potash, decompose a portion of it by means of muriatic acid, and observe whether the acid obtained fuses at 140°; if it does, it is pure margaric acid, but if it does not, it is contaminated with oleic acid, and the salt must therefore be again dissolved in hot alcohol and crystallized. We must proceed in this way till we obtain pure margarate of This salt is to be decomposed by muriatic acid, and washed and purified precisely in the way directed in the last. section for purifying stearic acid.

<sup>\*</sup> Chevreul sur les corps gros, p. 21.

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Properties.

The properties of margaric acid are very similar to those of stearic acid. The only characteristic difference is that it melts at 140°, while stearic acid does not melt till heated up to 158°. Margaric acid is exceedingly soluble in alcohol and ether, but like stearic acid it is insoluble in water. It reddens litmus paper, decomposes the alkaline carbonates, and forms a genus of salts to which the name of margarates has been given.

Chevreul analyzed a number of margarates. The atomic weight of margaric acid as derived from these analyses differs somewhat, as may be seen by the following table.

1. M	argar	rate of	potas	sh. .
Margaric a	-	•	•	34.24
Potash	•	•	•	6
2. A	<i>larga</i>	ırate q	f sode	<b>7.</b>
Margarie a	cid	•	•	32.81
Soda .	•	•	•	4
3. Me	argar	ate of	baryt	es.
Margaric a	cid	•	•	32.84
Barytes	•	•	•	9.5
4. A	<i>Iarga</i>	ırate q	f lime	2.
Margaric a	cid	•	•	31.61
Lime .	•	•	•	3.5
5. A	<b>I</b> arga	ırate q	f lead	<i>l</i> .
Margaric a	cid		•	33.48
Oxide of lo	ead		•	14

The mean of all these analyses gives us 32.996. We may therefore conclude it to be probable that the atomic weight of this acid is 33, which is a very little lighter than stearic acid.

Margaric acid in its common state is a hydrate compound of

It is obviously a compound of one atom acid and one atom water.

Composition.

Chevreul analyzed margaric acid by means of oxide of copper and obtained for the constituents.

Oxygen	•	•	8.937
Carbon	•	•	79.053
Hydrogen	•	•	12.010

100

The number of atoms which corresponds with these numbers, and suits the atomic weight of the acid, is the following:

3 atoms oxygen	•	•	3
35 atoms carbon	•	•	<b>20</b> 25
32 atoms hydrogen	•	•	4
€			
			33.25

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The atomic weight of stearic and margaric acids are the same. But margaric acid contains one atom more of oxygen, one atom less of carbon, and two atoms less of hydrogen. The number of atoms in this acid amounts to 70, while those in stearic acid amount to 72. Thus the differences between their characters, though not very striking, are accompanied by a decided difference in composition.

# SECTION XXVIII.—OF OLEIC ACID.

This acid was first described by Chevreul in 1813, under the History. name of graisse fluide. It may be obtained by the following process: Make a soap by uniting linseed or hemp oil with potash. Digest it in cold alcohol free from water. The oleate of potash will be dissolved, and the margarate of potash, which exists only in small quantity, will remain unacted on. Let the solution be evaporated, and let the residue be treated with the smallest quantity of absolute alcohol capable of dissolving it. Let it be separated from the small quantity of margarate of potash that remains undissolved. Let it then be mixed with water, and decomposed by boiling it with muriatic acid.

Oleic acid thus obtained has the appearance of a colourless Properties. oil. At the temperature of 66° its specific gravity is 0.898. A few degrees below 32° it congeals into a solid mass composed of needles. It has a slight odour and taste of rancidity. It may be volatilized in vacuo without alteration. It is insoluble in water. But in alcohol of the specific gravity 0.822, it dissolves in any proportion whatever. When water is mixed with the solution the acid separates. It decomposes the alkaline carbonates, strongly reddens litmus paper, and forms a class of salts, or rather soaps, to which the name of oleates has been given.

It combines in all proportions with stearic and margaric acids. When such a compound is treated with cold alcohol, much of the oleic acid is dissolved, together with a little of the stearic or margaric acid. When we treat the same compound with alcohol heated up to 140° the whole is dissolved. As the solution cools crystals of stearic acid or margaric acid are deposited, containing a little oleic acid. At a low temperature oleic acid unites with sulphuric acid without decomposition.

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When heated sufficiently in an open vessel, it burns like the fixed oils. When distilled there comes over first a colour-less oil. Then it boils, and the oil which comes over has a yellow colour. As the distillation proceeds the colour becomes darker, and at last carburetted hydrogen, carbonic acid, acetic acid, and some water, come over, and a very small quantity of charcoal remains in the retort. Nitric acid acts upon this acid as it does on the stearic, only with more rapidity, and the same kind of acid is formed. The following table exhibits the fusing point of mixtures, or combinations of oleic and margaric acid in different proportions, as determined by M. Chevreul.

Oleic acid,	Mrgaric acid.	Melting point.	Oleic acid.	Margaric acid.	Melting point.
99	1	32°	67	33	101°·75
98	2	35.5	66	34	102
97	3	37.5	65	35	103
96	4	41	64	36	103.3
95	5	44.5	63	37	104
94	6	46.5	62	38	104.25
93	7	48	61	39	106
92	8	50	60	40	106
91	9	57	59	41	107
90	10	62.5	58	42	107.5
89	11	64.5	57	43	107.5
88	12	70 •	56	44	108
87	13	75	55	45	108.5
86	14	<b>7</b> 8	54	46	109.5
85	15	79.75	53	47	109.75
84	16	81.5	52	48	110.75
83	17	83.3	51	49	111
82	18	85	50	50	111
81	19	88.75	49	51	111.5
80	20	88.75	48	<b>52</b>	112
79	21	89.5	47	53	113
78	22	91.5	46	54	113
77	23	93	45	55	114.3
76	24	94	44	56	115
75	<b>25</b>	96	43	57	115.25
74	26	96	42	58	115.75
73	27	97	41	59	115.75
72	28	97.75	40	60	116
71	29	98.5	39	61	116.5
70	30	99.5	38	62	118
69	31	100.4	37	63	118
<b>6</b> 8	32	101.3	36	64	118

`Oleic acid.	Margaric acid.	Melting point.	Oleic acid,	Margaric acid.	Melting. point.	
35	65	118·5°	17	83	124°	
34	66	118.5	16	84	124.75	
33	67	118.5	15	⋅85	125	
32	68	119	14	86	125.5	
31	69	119	13	87	125.5	
30	70	119.3	12	88	126.5	
29	71	149.3	11	89	126.5	
28	72	119.3	10	90	127.5	

127.5

129.5

130.5

130.5

127.75

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Atomic weight.

Chevreul analyzed several of the oleates and found the composition as follows:

l,	Oleat	te of p	otash.		
Oleic acid	•	•	•	<b>33·5</b>	•
Potash	•	•	•	6	
2.	Olea	te of	soda.		
Oleic acid	•		•	<b>33·6</b>	
Soda		•	•	4	
3.	Oleate	e of be	arytes.	•	
Oleic acid	•	•	•	31.87	
Barytes	•	•	•	9 <b>·5</b>	
4.	. Oled	ite of	lime.		
Oleic acid	•	•	•	36.26	
Lime	•	•	•	3.5	
5.	. Olea	ite of	lead.		
Oleic acid	•	•	•	32.94	
Oxide of l	ead		•	14	

The numbers after oleic acid represent the atomic weight of olcic acid, according to each analysis. The mean of all these numbers gives us 33.63 for the atomic weight of this acid.

From Chevreul's experiments it is obvious that oleic acid in its usual state, is a hydrate composed of 1 atom acid and 1 atom Now he found the constituents to be 100 acid and 3.95 water. water. If these numbers represent an atom of each, then the

119.75

120.5

121.5

122.5

122.5

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atomic weight of oleic acid is only 28.48. For 3.95:100:: 1.125:28.48. But little reliance can be put in this estimate, as doubtless the acid contained hygrometrical water.

Constituents.

Chevreul analyzed the acid by means of oxide of copper, and found its constituents to be

Oxygen	•	•	<b>7·699</b>
Carbon	•	•	80.942
Hydrogen	•	•	• 11-359
			100.000

The number of atoms corresponding with these weights and with the atomic weight of the acid, is as follows:

$2\frac{1}{2}$	atoms o	xygen	•	•	$2\cdot 5$
35	atoms c	arbon		•	<b>26</b>
30	atoms h	ydrogen	•	•	3.75
					32.25

This would make the atomic weight of oleic acid only 32.25; which is very nearly the mean of that deduced from the analyses of oleate of barytes, and oleate of lead.\*

### SECTION XXIX, --- OF PHOCENIC ACID.

History.

This acid was discovered by Chevreul in 1817, and described by him in 1818, under the name of *delphinic* acid. He afterwards changed the name to *phocenic* to avoid ambiguity, as the term *delphine* had been already applied to a vegetable principle. This acid exists in the oil of the porpoise (*delphinus globiceps*). It exists also in small quantity in *train oil*, and in the berries of the *viburnum opulus*.

To prepare it a soap must be made in the usual way of porpoise oil and potash. This soap is to be decomposed by tartaric acid, and the aqueous liquid freed from the stearic, margaric, and oleic acids is to be put into a close flask with more tartaric acid. By this means most of the potash is precipitated in the state of bitartrate. The liquid being distilled, phocenic acid comes over along with the water. Saturate the acid thus obtained with barytes, and evaporate the solution in order to obtain phocenate of barytes in the state of crystals. Put 100 parts of phocenate of barytes into a narrow glass tube shut at one end. Pour upon them 205 parts of aqueous phosphoric acid of the specific gravity 1·12, and agitate with a platinum wire. We

<sup>\*</sup> Chevreul sur les corps gras, p. 75.

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obtain, 1. Solid phosphate of barytes; 2. An aqueous liquid saturated with phocenic acid; and 3. Hydrated phocenic acid which swims upon the aqueous liquid. Draw off the phocenic acid by means of a sucker; and distil it by a gentle sand heat. The liquid in the receiver consists of two different layers. That next the bottom is small in quantity, and seems to be a simple solution of phocenic acid in water. The upper layer is much more abundant. It is a hydrated phocenic acid of the specific gravity 0.933, at the temperature of 82°. To obtain it quite pure, macerate it in a small retort over two or three times its weight of chloride of calcium, during four days. Then distil over a water bath till nothing more come over. The acid thus obtained has a specific gravity of 0.932 at 68°, and does not precipitate nitrate of silver.

Phocenic acid thus prepared is a limpid colourless liquid like Properties. a volatile oil. It does not congeal though cooled down to 16°. It boils when heated a few degrees higher than 212°. It may be distilled over without decomposition. It has a strong smell, quite peculiar; but bearing some analogy to that of acetic acid and of rancid butter. It stains paper like oil, and gives to those bodies a disagreeable smell like that of rancid train oil. It has a sharp acid taste, with an etherial impression.

At the temperature of 86°, 100 parts of water dissolve about 5.5 parts of this acid. Alcohol of the specific gravity 0.794 dissolves any quantity of it whatever. It dissolves in sulphuric and also in nitric acid without undergoing any alteration. It burns like a volatile oil. It combines with the different bases, and forms a genus of salts called *phocenates*. Chevreul analyzed several of these salts, and found the composition as follows:

1. Phocenate of barytes.

Phocenic acid		•	11.47
Barytes .	•	•	9.5
2. Phocen	ate of	<sup>c</sup> potas	h.
Phocenic acid		•	11.24
Potash .	•	•	6
3. Phoce	enate (	of lead	<b>7.</b>
Phocenic acid		•	11.62
Oxide of lead	_	_	14

The numbers after phocenic acid in each analysis represent the atomic weight of the acid. The mean derived from the three preceding analyses is 11.44. The atomic weight derived from phocenate of lime is 10.79.

Chevreul subjected the acid itself to analysis, by heating

composition. phocenate of tead with oxide of copper. He obtained for the constituents of the acid,

100.00

The number of atoms which correspond with these constituents, and with the atomic weight of the acid, is as follows,

11.4375

This number almost coincides with that deduced from the analyses of the phocenates. Perhaps we might, without impropriety, leave out the half atom of hydrogen, in which case the atomic weight would be reduced to 11.375.

The hydrated phocenic acid, according to Chevreul's analysis, is a compound of

Phocenic acid . . . 11.5
Water . . . . 1.137

We see from this that it is a compound of 1 atom acid and 1 atom water.\*

#### SECTION XXX. -- OF BUTYRIC ACID.

History.

The existence of this acid was announced by Chevreul in 1814; but it was not till the year 1818 that he succeeded in obtaining it in a state of purity. It may be obtained by the following process:

Butter is to be converted into a soap precisely in the way described when treating of stearic acid. The soap is to be decomposed, and distilled exactly as was described in the last section for procuring phocenic acid. The distilled liquid is to be saturated with barytes and evaporated. The matter obtained is a mixture of butyrate, capreate, and caprate of barytes. It must be digested in 2.77 times its weight of cold water for 24 hours. The undissolved portion is to be again digested 24 hours in 2.77 times its weight of water, and this must be repeated till nothing remains undissolved but carbonate of barytes. As butyrate of barytes is soluble in 2.77 times its weight of cold

<sup>\*</sup> Chevreul, sur les corps gras, p. 99.

Class I. Div. II.

water, the whole of it is found in the first solution mixed with a little of the two other salts. The next solution consists chiefly of caproate, and the last of caprate of barytes as the least soluble salt of the three. By repeated crystallizations the butyrate of barytes is freed from the admixture of the other salts, and obtained in a state of purity. The butyrate of barytes is decomposed in a glass tube by means of phosphoric acid, and the barytic acid obtained precisely in the same way as the phocenic acid is obtained, and as the process was described in the last section.\*

Butyric acid thus prepared is a colourless liquid, which does Properties. not congeal though cooled down to 16°. It boils when heated a few degrees higher than 212°. At 50° its specific gravity is 0.9675. Its odour is analogous to that of acetic acid and rancid butter conjoined; somewhat similar to that of phocenic acid, but not so strong. It stains paper like oil, but the stain disappears by the evaporation of the acid. It has a strong acid taste, leaving an impression of sweetness. Like phocenic acid it whitens the part of the tongue to which it is applied.

Water dissolves it in all proportions. A solution of two parts acid in one part of water has a specific gravity of 1.00287. Alcohol of the specific gravity 0.794, dissolves it in all proportions. The solution has an etherial odour of pippins (pomme de reinette). Concentrated suphuric acid dissolves it at 60° with the evolution of heat. Cold nitric acid of the specific gravity 1.312, dissolves it also without any alteration. The solution has an etherial smell. When mixed with hog's-lard, it gives it an exact resemblance to butter. But when exposed to the air the acid gradually escapes, and the lard remains unaltered. Butyric acid burns like the volatile oils.

It combines with bases and forms a genus of salts called butyrates. The following table exhibits the constitution of several of these salts as analyzed by Chevreul.

1. Bu	tyrate	of ba	rytes.		Atomic
Butyric acid	•	•	•	9.73	weight
Barytes	•	•	•	$9 \cdot 5$	
2. <i>E</i>	Butyra	te of l	lime.		
Butyric acid	•	•	•	9.46	
Lime .			•	3.5	

<sup>\*</sup> The reader will find a detailed statement of the processes in Chevreul sur les corps gras, p. 215.

Chap, I.	3. Butyro	3. Butyrate of potash.						
	Butyric acid	•	•	9.8				
	Potash .		•	6				
	4. Butyr	4. Butyrate of soda.						
	Butyric acid	•	•	10				
	Soda	•	•	4				
	5. Butyr	5. Butyrate of lead.						
	Butyric acid	•	•	9.14				
	Oxide of lead	•	•	14				

The mean of these numbers gives 9.62 as the atomic weight of butyric acid.

Chevreul analyzed butyric acid by heating butyrate of lead with a sufficient quantity of oxide of copper. He found it resolvable into the following constituents,

Oxygen	•	•	•	30.17
Carbon	•	•	•	62.52
Hydrogen	_	_		7.01

The number of atoms best agreeing with this constitution, and with the atomic weight deduced from the analysis of the buty-rates, is the following,

3 atoms oxygen	•	•	3
8 atoms carbon	•	•	6
5 atoms hydrogen	•		0.625

9.625

Butyric acid in its ordinary state is composed, according to the analysis of Chevreul, of

> Butyric acid . . . 9.625 Water . . . 1.116

is obviously a compound of 1 atom acid and 1 atom water.

#### SECTION XXXI. -- OF CAPROIC ACID.

History.

This acid was discovered by Chevreul in 1818. It was named from capra, a goat, because it exists in the butter of the cow and goat.

Caproic acid is obtained in the state of caproate of barytes by the processes described in the last section. The 2d solution in the 2.77 of water consists chiefly of caproate of barytes, and it is to be freed from the small quantity of caprate of barytes which it contains by repeated crystallizations and solutions. One part of caproate of barytes is to be put into a glass tube with 0.2963 of sulphuric acid diluted with its own weight of

<sup>\*</sup> Chevreul sur les corps gras, p. 115.

water. After 24 hours the caproic acid which has separated is to be drawn off. It is to be digested for 48 hours on its own weight of chloride of calcium and then distilled.

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Caproic acid is a colourless liquid, resembling a volatile oil Properties. in appearance. It does not congeal at 16°, and it may be distilled over without decomposition. At 79° its specific gravity is 0.922. Its taste is a sharp acid, leaving a sweetish impression on the palate. Its smell resembles that of weak acetic acid, or rather sweat. It whitens those parts of the tongue to which it is applied.

At the temperature of 45°, 100 parts of water dissolve 1.04 of caproic acid. But alcohol of the specific gravity 0.794, dissolves it in all proportions. It combines without decomposition with concentrated sulphuric acid, and with nitric acid of the specific gravity 1.312. It burns with flame like the volatile oils.

It combines with bases, and forms a genus of salts called caproates. Chevreul analyzed several of these caproates, and obtained the following results:

1. Ca <sub>1</sub>	proat	e of $b$	arytes.	•	Atomic weight,
Caproic acid		•	•	13.11	
Barytes	•	•	•	9.5	
2. Ce	aproa	te of	lime.		
Caproic acid		•	•	13:34	
Lime	•	•	•	3.5	
<b>3.</b> Ca	proa	te of p	otash.		
Caproic acid		•	•	14.18	
Potash	•	•	•	6	
4. Ca	aproa	te of	soda.		
Caproic acid		•		14:36	
Soda .	•	•	•	4	

The mean of these analyses gives as 13.75 for the atomic weight of caproic acid. It was analyzed by Chevreul by means of oxide of copper. He found the constituents to be

Composition.

Oxygen	. •	•	•	<b>22</b> ·67
Carbon	•	•	•	68.33
Hydrogen	•	•	•	9.00

100.00

The atoms coming nearest to these numbers, and corresponding best with the atomic weight deduced from the analyses of the salts, are the following: 3 toms oxygen . . . 3
12 atoms carbon . . . 9
10 atoms hydrogen . . . 1.25

13.25

Caproic acid, in its natural state, is a hydrate composed of

It is obviously, therefore, a compound of 1 atom acid and 1 atom water.\*

### SECTION XXXII. -- OF CAPRIC ACID.

History.

This acid was discovered by Chevreul in 1818, at the same time with the caproic: and the name was also derived from capra, because, like the two preceding acids, it exists in the butter of the cow and the goat.

It exists in the aqueous solutions of butyrate of barytes, described in the two last sections, as dissolved in 2.77 water at different times. The greatest portion of the third solution consists of caprate of barytes. It is purified by repeated crystallizations and solutions. And the pure caprate of barytes may be either decomposed by means of phosphoric acid or sulphuric acid, in the way described in the two last sections.

Properties.

Capric acid is solid, and has the shape of colourless needles at the temperature of 62°. At 64° it melts into a transparent colourless liquid resembling a volatile oil. Its specific gravity at 64° is 0.9103. Its taste is acid and hot. It has the smell of caproic acid with a slight odour of the goat. It is very little soluble in water at the temperature of 68°, 1000 parts of water dissolving only one part of capric acid; but alcohol dissolves it in all proportions.

It forms a genus of salts called *caprates*, two of which were analyzed by Chevreul with the following results:

# 1. Caprate of barytes.

Capric acid		•	•	16.83
Barytes	•	•		9.5

## 2. Caprate of strontian.

Capric acid		•	•	17.1
Strontian	_			6.5

The mean of these two analyses gives 16.96 for the atomic weight of capric acid.

<sup>\*</sup> Chevreul sur les corps gras, p. 134.

This acid being analyzed in the usual manner by Chevreul, was found composed of

Oxygen . . . 16·25 Carbon . . . 74·00 Hydrogen . . . 9·75

100.00

The atoms corresponding best with these proportions, and Composition. approaching the atomic weight deduced from the salts, are the following:

 3 atoms oxygen
 .
 .
 3

 18 atoms carbon
 .
 .
 13.5

 14 atoms hydrogen
 .
 1.75

18.25

But if 18.25 be the atomic weight of the acid, Chevreul's analyses of the caprate do not constitute very near approximations to the truth.\*

#### SECTION XXXIII. - OF HIRCIC ACID.

This acid was discovered by Chevreul during his researches on fatty bodies. But its properties have been very imperfectly examined.

To obtain it soap made of mutton tallow is to be decomposed by tartaric or phosphoric acid. The aqueous liquid being distilled the hircic acid passes over with the water. Neutralize it with hydrate of barytes, evaporate to dryness, and decompose the *hircate* of barytes by sulphuric acid previously diluted with its own weight of water.

It is a colourless liquid which does not congeal at 32°. It Properties, is lighter than water; has a smell analogous to that of acetic acid. It is volatile, very little soluble in water, but very soluble in alcohol. It reddens strongly litmus paper.

Hircate of potash is a deliquescent salt. Hircate of barytes is not very soluble in water, and is composed of

According to this analysis the probable atomic weight of hircic acid is 12 or 12.25.+

### SECTION XXXIV. -- OF RICINIC ACID.

This acid was discovered in 1827 by MM. Bussy and History. Lecanu. The method of obtaining it is as follows:

<sup>\*</sup> Chevreul sur les corps gras, p. 143.

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Castor oil (deum ricini) is distilled over in a retort, and the product of the distillation is boiled with water to free it from a portion of acetic acid, and to get rid of a volatile oil with which it is mixed. The portion remaining is a mixture of ricinic and elaiodic acids. Of this mixture one-third part is to be distilled over. This portion becomes solid at the temperature of 50°. It is to be subjected to pressure between folds of bloating paper which will imbibe elaiodic acid, with which it is still contaminated. It is now ricinic acid in a state of purity.

Properties.

Ricinic acid thus prepared is a white solid having a pearly lustre. At 72° it melts into a colourless oil which assumes a crystalline texture on cooling. It may be volatilized in a retort by a moderate heat without decomposition. It has a strong and sharp taste. It is insoluble in water, but soluble in alcohol and ether. These solutions redden litmus paper. Its constituents when in crystals, as determined by the analysis of Bussy and Lecanu, are as follows:

Oxygen	•	•	16.58
Carbon	•	•	73.56
Hydrogen	•	•	9.86

#### 100.00

It would appear from the experiments of the same chemists, that ricinate of magnesia is composed of

Ricinic acid	•	•	<b>25</b>
Magnesia			2.5

This makes its atomic weight 25. The number of atoms corresponding best with these two analyses is the following:

Composition.

4 atoms oxygen	•	•	. 4
24 atoms carbon	•	•	18
24 atoms hydrogen			2.75

#### 24.75

But new researches are wanting to enable us to determine how near these proportions approach to the true atomic weight of the anhydrous acid; analogy leads to the conclusion that the crystallized ricinic acid contains an atom of water.

Salts.

Ricinic acid when assisted by heat decomposes the alkaline carbonates. Ricinate of potash resembles soap. It is soluble in water and alcohol. It is decomposed by calcareous salts and also by common salt. The *ricinate of soda* resembles that of potash. Ricinate of lime is insoluble in water. Ricinate of lime is insoluble in water.

nate of magnesia is insoluble in water; but very soluble in several other ricinates.\*

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#### SECTION XXXV. OF ELAIODIC ACID.

This acid was also discovered by MM. Bussy and Lecanu during their researches on castor oil: but its properties have been very superficially examined. It may be obtained by the following process:

The castor oil is to be distilled and treated as described in the last section, till a mixture of ricinic and elaiodic acid is obtained as there stated. This mixture is to be cooled to 32°, and then subjected to pressure between folds of bloating paper. The ricinic acid remains while the elaiodic acid is imbibed by the paper. It is to be dissolved in alcohol, and freed from the small quantity of ricinic acid which it contains, by repeated evaporations and crystallizations.

Elaiodic acid is a yellow coloured oil, congealing into a solid Properties. mass when cooled down a few degrees below 32°. It has a sharp taste, and has a slight empyreumatic smell. It combines easily with bases. The elaiodates of potash and soda dissolve readily in water and alcohol. Those of magnesia and lead are insoluble in water, but easily soluble in alcohol.

This acid is insoluble in water; but dissolves with facility in alcohol and ether.+

#### SECTION XXXVI. -- OF CEVADIC ACID.

This acid was discovered in the seeds of the veratrum saba-History. dilla, called cevadille by Pelletier and Caventou during their examination of that vegetable substance in the year 1820.† It was obtained by them in the following manner:

The seeds of the veratrum were macerated in ether, the action of which was assisted by heat. The ether when drawn off had assumed a yellow colour. This liquid being distilled by the heat of a water bath, the water passed off colourless and left a yellow unctuous matter, insoluble in water and soluble in alcohol and ether. It reddened vegetable blues, and had a strong and peculiar odour. To determine its nature it was converted into a soap by boiling it with potash ley. This soap was decomposed by adding to it an excess of tartaric acid. Flocks of unctuous matter separated which were composed of oleic and

<sup>\*</sup> Jour. de Pharmacie, xiii. 68.

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tartaric acids. The filtered liquid had a yellow colour, together with an acrid and acid taste. When subjected to distillation there came over an aqueous liquid having an acid taste and a strong smell, while cream of tartar and various other vegetable principles remained in the retort. Into the liquid thus obtained barytes water was poured, which destroyed the acidity of the liquid without entirely removing the smell. Being evaporated to dryness a substance was obtained of a fine white colour, composed of cevadic acid united to barytes. A sufficient quantity of phosphoric acid was added to saturate the barytes, and a gentle heat being applied, the cevadic acid sublimed, and was thus obtained in a separate state.

Properties.

Cevadic acid thus obtained, is a solid substance of a fine white colour, and crystallized in needles. It melts when heated to the temperature of 68°. Its smell has a good deal of resemblance to that of butyric acid; but is not quite the same. It sublimes at a moderate heat. It is soluble in water, alcohol, and ether. It combines with the different bases and forms a genus of salts called *cevadates*, which have been very imperfectly investigated. They retain a portion of the peculiar smell which distinguishes the acid.

This acid approaches nearest to the butyric and phocenic; but is sufficiently distinguished by the concrete state in which it exists at temperatures below 68°.

#### SECTION XXXVII. -- OF CROTONIC ACID.

History.

This acid was discovered by Pelletier and Caventou about the year 1819,\* during their examination of what they considered as the seeds of the Iatropha Curcas, but which were afterwards found to be the fruit of the croton tiglium, a tree which grows in the Moluccas, and which yields croton oil, so much employed of late years in this country as a purgative. is a very poisonous oil, which had been much employed by medical men during the 17th century, but which had gone out of use in consequence of the uncertainty of its operation, and the fatal effects which it produced when given in too large doses. To obtain crotonic acid, the croton seeds are digested in ether or The infusion being distilled leaves a combination of alcohol. This oily matter being boiled with water oil and crotonic acid. and magnesia to dryness and digested in ether, the oil is removed, and there remains a combination of crotonic acid and magnesia, which being mixed with phosphoric acid, and distilled, crotonic acid passes over.

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But by this process very little crotonic acid is obtained, because most of it remains united to the oil. The best way of proceeding, therefore, is to convert the oil into a soap by boiling it with potash ley. The soap is to be decomposed by tartaric acid, the liquid is to be filtered and distilled in a well luted apparatus. The liquid that passes over, and which contains the crotonic acid, is to be neutralized with barytes water, and evaporated to dryness. The crotonate of barytes being now mixed with highly concentrated phosphoric acid and distilled, the crotonic acid is sublimed.

Crotonic acid thus obtained congeals when cooled down to Properties. 23°. When heated a few degrees above 32° it sublimes in a vapour, having a strong smell, and acting pretty strongly on the nostrils and eyes. It reddens litmus paper. The taste is sharp, and its properties are very poisonous. It dissolves in water, alcohol, and ether. It is doubtless this substance which gives to croton oil its cathartic and poisonous qualities.

Crotonate of potash crystallizes in rhomboidal prisms, which are not altered by exposure to the air. It dissolves with difficulty in alcohol of the specific gravity 0.85. Crotonate of barytes is soluble in water, and when the solution is evaporated, either forms pearly crystals, or falls in the state of a white powder. Crotonate of magnesia may be obtained in small grains very little soluble in water. Crotonate of ammonia precipitates iron from the sulphate of an isabella yellow colour. It precipitates the salts of lead, copper, and silver white.

#### SECTION XXXVIII. OF AMBREIC ACID.

Ambergris is a substance found floating in the sea, most History. commonly near the coasts of India, Africa, and Brazil, usually in small pieces, but sometimes in masses of 50 or 100 pounds weight. It is generally considered as a concretion formed in the intestines of the physeter macrocephalus, or spermaceti whale. It is a soft substance, which swims in water, having an ash gray colour with brownish yellow and white streaks. It was examined in considerable detail by Bouillon La Grange.\* He extracted from it, by means of alcohol, a white substance, to which he gave the name of adipocire, because he considered it as the same with the substance which makes its appearance

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when dead bodies in great numbers putrefy together, and to which the name adipocire had been given by Fourcroy. But being examined in 1820 by Pelletier and Caventou, they found reason to consider it as a peculiar substance, different from every other. On that account they distinguished it by the name of ambreine.\*

Ambreine is easily obtained by digesting ambergris in hot alcohol, of the specific gravity 0.827, filtering the liquid, and leaving it to itself. The ambreine is deposited in a kind of stalactitical state, retaining a great deal of alcohol, which may be driven off by evaporation, when the bulk of the ambreine is very much diminished. It has a fine white colour, is tasteless, and has at first a sweet smell, which is dissipated by repeated crystallizations. It is insoluble in water, but dissolves readily in ether and alcohol of the temperature of 50°. It does not redden litmus paper. It melts at 86°. When heated above 212° it becomes brown, exhales a white smoke, and is partly decomposed. The white smoke consists of ambreine unaltered. It is incapable of forming soap with alkalies.

Pelletier and Caventou found that when treated with nitric acid and heat it dissolves and swells, while abundance of deut-oxide of azote is driven off. The ambreine becomes first green and then yellow. It is now converted into a peculiar acid, to which Pelletier and Caventou, the discoverers, have given the name of ambreic acid.

To obtain this acid we have only to heat ambreine with nitric acid till it ceases to undergo any farther change. Then evaporate cautiously to dryness; wash the dry mass with cold water to remove as much of the acid as possible, then boil it with a little carbonate of lead. If we now wash it with cold water till the solution ceases to retain any traces of lead, we are certain that the nitric acid has been completely removed. We have only now to digest the residue in alcohol and set the solution aside; the ambreic acid crystallizes in small plates.

Properties.

Ambreic acid when in masses is yellow, when much divided it appears white. It has a peculiar smell, quite different from that of ambergris. It reddens litmus paper. When heated, it is decomposed without furnishing any ammonia. It remains solid when heated to 212°, while cholesteric acid fuses at 136°. This constitutes a striking distinction between them.

Ambreic acid is also much less soluble than cholesteric in

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It is soluble only to a very small extent in alcohol and ether. water, though hot water dissolves more of it than cold water. This acid combines with bases, and forms a genus of salts called ambreates. With potash it combines in two proportions. binambreate is insoluble in water, but soluble in alcohol. The neutral ambreate dissolves in water. This salt throws down vellow precipitates when dropped into solutions of chloride of calcium, chloride of barium, sulphate of copper, sulphate of iron, nitrate of silver, acetate of lead, chloride of mercury, of tin, and of gold.

No attempts have been made to determine the atomic weight of this acid, or to analyze it. But it is obvious from the phenomena of its decomposition that its only constituents are oxygen, carbon, and hydrogen.

#### SECTION XXXIX. --- OF CHOLESTERIC ACID.

Poulletier de la Salle first examined one of the most common Cholesterine. species of biliary calculi, and by means of alcohol extracted a white substance in plates, somewhat like spermaceti. Fourcroy afterwards, considering it as analogous to the soapy matter extracted from the dead bodies which had been left in great numbers in pits in the burial ground of the Innocents in Paris, and on that account called it adipocire. Chevreul examined it in 1816, showed that it possesses peculiar properties, and on that account gave it the name of cholesterine.\*

It continues solid till heated up to the temperature of 278°, Properties. when it melts. On being allowed to cool it crystallizes in plates radiating from a centre. It is tasteless and destitute of It is insoluble in water, but 100 parts of boiling alcohol of the specific gravity 0.817 dissolve 18 parts of it, but on cooling, the greatest part of the cholesterine is deposited in brilliant scales. It has no acid properties, and is incapable of being converted into soap when boiled with the alkalies. It is composed, according to the analysis of Chevreul, of

Composition.

Oxygen	•	•	· •	3.025
Carbon	•		•	85.095
Hydrogen				11.880

100.000+

Now the smallest number of atoms that correspond with these proportions is the following:

<sup>\*</sup> From χολη (bile), and σθερεφ (solid). † Sur les Corps gras, p. 153.

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latom oxygen .	•	1
38 atoms carbon .	•	28.5
32 atoms hydrogen	•	4
•		
		33.5

So that the atomic weight of cholesterine cannot be less than 33.5.

Pelletier and Caventou ascertained in 1817 that when cholesterine is heated with its own weight of nitric acid till no more deutoxide of azote is disengaged, there separates a yellow matter which possesses acid properties, and to which they gave the name of cholesteric acid. When the acid liquid is diluted with water, an additional quantity of cholesteric acid separates. By repeated washings in water (in which it is scarcely soluble) it may be freed from nitric acid and rendered quite pure.

Cholesteric acid.

Cholesteric acid has an orange colour when in mass, but if we dissolve it in alcohol and allow it to crystallize, we obtain it under the form of white needles. Its smell is somewhat analogous to that of butter. Its taste is styptic, but exceedingly slight. It is lighter than water, but heavier than alcohol. It melts when heated to 136°. At a temperature somewhat higher than that of boiling water it undergoes decomposition, being converted into an oil, water, carbonic acid, and carburetted hydrogen.

It combines readily with the bases, and forms salts called cholesterates. They have all more or less colour. Those of potash, soda, and ammonia, are very soluble in water and deliquescent. They do not crystallize, and are insoluble in alcohol and ether. All the other cholesterates examined are very little or not at all soluble. Cholesterate of barytes is red, and very little soluble. It is composed, according to Pelletier and Caventou, of

Atomic weight.

Cholesteric ac	id	•	•	16.88
Barytes	•	•	•	9.5

Cholesterate of strontian is insoluble in water, and has an orange colour. According to the analysis of the same chemists, it is composed of

Cholesteric acid . . . 17.57 Strontian . . . 6.5

The cholesterate of lime is very little, and that of magnesia not at all soluble in water. The cholesterate of alumina has a fine red colour while moist, but when dry it becomes darker coloured, and has lost its beauty.

Cholesterate of lead is brick red, and is composed, according to the analyses of Pelletier and Caventou, of very nearly

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Now 56 represents four atoms of oxide of lead. The salt must therefore be a tetraki-cholesterate of lead.

The atomic weight of cholesteric acid, deduced from the three preceding analyses, varies too much to admit of any very accurate deductions. By cholesterate of lead it is 20, while cholesterate of barytes makes it only 16.88. The mean of the three analyses makes the atomic weight 18.15. Probably therefore it is about 18.

When cholesterate of potash is dropped into nitrate of mercury, a black precipitate falls, while with the pernitrate of mercury the precipitate is red. With copper salts an olive coloured precipitate is obtained. The cholesterate of zinc has a fine red colour, and is little soluble in water.\*

#### SECTION XL .- OF PINIC ACID.

In the year 1826 M. Baup inserted a notice in a periodical History. work,† that he had discovered pinic acid in the resin called colophon, crystallized in triangular plates, soluble in 4 times its weight of alcohol, but insoluble in water, while the resin of the pinus abies yielded another acid crystallized in square plates, and soluble in  $7\frac{1}{2}$  times its weight of alcohol, to which he gave the name of abietic acid. He states nothing farther respecting these acids in his short notice above referred to, so that it is impossible to say whether his acids be the same as those of Unverdorben.

Unverdorben had been occupied with the examination of resins for several years. He had shown, at least as early as the year 1825,‡ that colophon possesses the characters of an acid. His account of pinic acid appeared in 1827.§ He has shown that resins are divisible into two sets, namely, those which have acid properties, and those which are indifferent. The resins from the pine tribe belong to the first set, but they are seldom pure, being generally mixed with foreign bodies and with resinous substances which are indifferent. Pinic acid may be procured from colophon or common white resin, and from common and Venetian turpentine. To obtain it pure, we may proceed as follows:

<sup>\*</sup> Ann. de Chim. et de Phys. vi. 401. † Ibid. xxxi. 108. † Poggendorf's Annalen, vii. 311, and viii. 397, 477. § Ibid. xi. 47.

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Distil Venetian turpentine with water, frequently renewing that liquid, till both the more and less volatile oil of turpentine has passed over. Dissolve the residual resin in alcohol, and mix the liquid with a solution of acetate of copper in alcohol. Pinate of copper precipitates, which must be collected on a filter and washed with absolute alcohol. Then dissolve it in alcohol containing muriatic acid, and mix the solution with its own weight of water. Pinic acid falls down, and is to be freed from alcohol by boiling it in water. Pinic acid thus obtained still contains mixed with it a small quantity of resin not soluble in alcohol.

Properties.

Pinic acid is hard and brittle, and becomes electric when rubbed. When procured from turpentine it is transparent and colourless. It has no smell, but is distinguished by a bitterish taste. When fused, it assumes a brown colour in consequence of the formation of colophonic acid. By an increase of the heat it flows thin, and when made to boil, at least one-fourth of it is converted into colophonic acid. When distilled in a small glass retort it gives out a little carbonic oxide mixed with carburetted hydrogen gas, with a yellowish tar, owing to the mixture of resic acid and a little water. This water contains acetic acid and a little resin, with volatile oil and odorin. The tar contains acetic acid and some colophonic acid, mixed with much pinic acid. When the distillation takes place in a large retort, almost all the pinic acid is decomposed.

It is insoluble in water, but soluble in alcohol and ether. It dissolves also in bisulphuret of carbon. It dissolves also in concentrated sulphuric acid, and is again precipitated by water. It dissolves also in oil of turpentine. When fused with the alkaline carbonates, it drives off the carbonic acid very rapidly.

Pinic acid acts pretty powerfully as an acid, but in order to judge of its activity it must be dissolved in ether. If to an etherial solution of pinic acid we add carbonate of copper, the carbonic acid is gradually driven off with an effervescence, and the oxide of copper dissolves in the solution. When acetate of copper in fine powder is added to such an etherial solution at the temperature of 60°, the salt is gradually decomposed, and the oxide of copper combining with the pinic acid colours the liquid green. Pinate of copper is decomposed by muriatic acid, sulphuric acid, nitric acid, and phosphoric acid. The carbonate, acetate, and most of the volatile vegetable acid compounds of oxide of copper, are decomposed by pinic acid; but the sulphate, nitrate, and phosphate of copper, are not altered

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by it. It is curious that the etherial solution of pinic acid does not act upon black oxide of copper; at least it scarcely acquires a green colour after some weeks' digestion: neither does it decompose or dissolve carbonate of lime. But acetate of lime is readily decomposed by the alcoholic solution of pinic acid. Muriate of lime is imperfectly decomposed when fused with And the same remark applies to muriate of magnesia. The carbonates of potash and soda are very readily decomposed when boiled in a solution of pinic acid in oil of turpentine.

Acetic acid partially decomposes pinate of copper. remains a mixture of pinic acid and pinate of copper. the other hand pinic acid, in the state of a fine powder, decomposes acetate of copper: acetic acid is disengaged and pinate

of copper formed.

Pinic acid combines with the different bases and destroys their alkaline qualities. The pinates formed are usually neutral. They resemble resin in their appearance, and none of them are capable of crystallizing. They are soluble in alcohol and ether, and the alkaline pinates also in water. The alkaline pinates may be formed by digesting the solution of pinic acid in ether over an alkaline carbonate. The earthy and metalline pinates by double decomposition by adding a solution of salt containing the base to a solution of pinate of potash or soda.

Unverdorben analyzed several of the pinates in order to determine the atomic weight of pinic acid. The results were as Atomic weight. follows:\*

1.	Pinate	$e$ of $oldsymbol{\mathit{I}}$	ime.	
Pinic acid	•	•	•	67.64
Lime	•	•	• .	3.5
2. P	inate q	f Ma	gnesio	τ.
Pinic acid	•	•	•	67 <b>·5</b>
Magnesia	•	•	. •	2.5
3. 1	Pinate	of ba	rytes.	
Pinic acid	. •	•	•	<b>73</b>
Barytes	•	•	•	9.5

<sup>\*</sup> These analyses are derived from the statements of Leopold Gmelin in his Handbuch der Theoretischen Chemie, vol. ii. p. 523, &c. They are given by Unverdorben while giving an account of the combination of colophon with bases, Poggendorf's Annalen, vii. 312. Gmelin says that Unverdorben himself rates the atomic weight of pinic acid at 55.2, but I do not know from what data he has drawn his conclusions.

Chap.	ı.
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4.	Pinat	e of s	oda.	
Pinic acid	•	•	•	<b>52·63</b>
Soda		•	•	4
5. <i>1</i>	Pinate	of po	tash.	
Pinic acid		•	•	65.7
Potash			•	6

The pinates of barytes and soda deviate so far from the others that we cannot include them. The mean atomic weight of pinic acid derived from the others is 66.95. We may, therefore, pitch upon 67, as not far from the truth.

## Of Colophonic Acid. .

History.

Colophon is the name given on the continent to the brown, brittle, semitransparent resin, which remains when turpentine has been subjected to distillation in order to obtain oil of tur-Unverdorben first showed that it was capable of neutralizing alkaline bodies, and therefore possessed properties analogous to acids. Indeed as it has been long employed in this country in the manufactory of soap, this inference might have been very naturally drawn, though I am not aware that any chemist in this country actually drew it. From Unverdorben's experiments it appears that pinic acid when strongly heated becomes brown, and is partially converted into colophonic acid. Colophonic acid seems, therefore, very closely connected with pinic acid; and Unverdorben has nowhere pointed out in what the difference between them consists. According to the analysis of Gay-Lussac and Thenard, colophon is composed of

Hydrogen		•	•	10.719
Carbon	•	• .	•	<b>75</b> ·944
Oxygen	•	•	•	13.337

100.000

which Unverdorben, from his experiments on the atomic weight of colophonic acid, has resolved into

119 atoms hydrogen		•	•	14.875
69 atoms carbon	•	•	•	51.75
9 atoms oxygen		•	•	9

75.625

This would make its atomic weight 75.625. But the atomic weight derived from his analyses of several colophonates comes nearly to the same number as that given in the last section for pinic acid. In fact the data from which that number was got,

results from the analysis of colophonates. Now the number of atoms corresponding with the atomic weight of 67, and with \_ the analysis of colophon by Gay-Lussac and Thenard, are

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64 atoms hydrogen	•	•	8
67 atoms carbon	•	•	50.25
9 atoms oxygen	•	•	9
			<del>*************************************</del>
			67.95

This, therefore, ought to represent the atomic constitution of colophonic acid, according to the data furnished by Unverdorben.

M. Unverdorben'states that colophon is not pure colophonic acid, but that it is contaminated by a mixture of an indifferent resin. But he has no where given a process by which it may be purified.

When thrown down from an alkaline solution by means of an acid, it is in the state of a hydrate, composed of 100 colophon and 13·1 water. This is very nearly

l atom colophon	•	•	67
8 atoms water	•	•	9
			76

#### SECTION XLI .- OF SILVIC ACID.

This acid forms one of the constituents of the common tur- History. pentine which exudes from the pinus silvestris. Hence the name given it by Unverdorben. He considers it as identical with the crystalline substance which Riess met with in white pitch,\* and likewise with the abietic acid of Baup, mentioned in the last section. It may be obtained pure by the following process:

Mix common turpentine with water, and distil to get rid of the volatile oil. Digest the residual matter in cold alcohol of the specific gravity 0.883, which will leave undissolved most of the silvic acid, mixed with a small quantity of pinic acid. Then boil this undissolved residue in twice its weight of alcohol of the specific gravity 0.883. As the solution cools the silvic acid precipitates still mixed with about four per cent. of pinic acid, but from this it may be freed by repeated solutions in the boiling hot alcohol of 0.883. Or if the precipitate be digested repeatedly in cold alcohol of the specific gravity 0.883, the pinic acid will be dissolved, while the greatest part of the silvic acid

<sup>\*</sup> Jahrbuch des Polytechnischen Instituts zu Wien, i. 435.

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will remain unaltered. But the easiest way of obtaining it pure is to dissolve the impure acid in twice its weight of absolute alcohol, containing  $\frac{1}{20}$ th of its weight sulphuric acid. When the solution cools the silvic acid shoots into large crystals, free from pinic and sulphuric acid, provided they be washed in alcohol of the specific gravity 0.883.

Properties.

Silvic acid is transparent and colourless, and has the form of low four-sided prisms, terminated by a four-sided pyramid. When heated it melts into a colourless mass, without any appearance of crystallization . When scratched with a hard body it breaks with a slight crack, as happens also to pinic acid. It is nearly as hard as colophon. When rubbed it becomes electric. When heated it becomes soft and thready. It fuses at the temperature of about 212°.

It is insoluble in water, but dissolves in alcohol and ether.

When heated to 336° it gives out no water. When raised to a higher temperature than this in a retort, it becomes first thick and then quite fluid, gives out a little water and empyreumatic oil; it then boils and gives out no more water, but is converted into oil at first limpid but becoming gradually thick, while at the same time a little gas is disengaged. If the process be stopped when two-thirds of the matter has passed over the residue is light brown, and consists of a mixture of silvic acid, pinic acid, a little resin similar to pinic acid, and a neutral resin soluble in absolute alcohol, from which it falls when left to spontaneous crystallization in colourless crystalline flocks.

When silvic acid is boiled in nitric acid, it slowly undergoes decomposition, being changed into a yellow resin, which when dissolved in alcohol strongly reddens litmus paper. This altered resin possesses also the properties of an acid, and combines with the different bases. Silvic acid dissolves readily in sulphuric acid. The solution is yellow brown, and water throws down from it a mixture of a little silvic acid with a great deal of pinic acid.

Silvic acid may be obtained in the state of a hydrate by throwing it down from its solution in potash by means of a stronger acid. The water does not separate unless the silvic acid be mixed with oxide of lead.

Unverdorben, to whom we are indebted for all the facts respecting this acid which have been stated, examined also a number of the *silvates*, and determined their properties. But as he made no attempt to analyze any of these salts, we are still

ignorant of the atomic weight of this acid. It is doubtless high.\*

Class I. Div. II.

### SECTION XLII. - OF CARBAZOTIC ACID.

It was discovered by Haussmann in 1788, that when indigo History. is treated with nitric acid, it is converted into a yellow coloured and bitter tasted substance, which has been ever since known by the name of bitter principle of indigo.† It was afterwards examined by Fourcroy and Vauquelin.† And at a still latter period by Chevreul, who endeavoured to show that it was a compound of nitric acid with a peculiar principle derived from indigo. In 1827 an elaborate set of experiments was made on it by M. Liebig, who demonstrated it to be a peculiar acid composed of azote, carbon, and oxygen; but without any trace of nitric acid, and to which he gave the name of carbazotic acid. Ilis mode of obtaining this acid in a state of purity was as follows:

The best indigo reduced to a coarse powder is digested with eight or ten times its weight of nitric acid of mean strength at a very moderate temperature. It dissolves with a copious emission of nitrous fumes, while it froths up very considerably. After the violent ebullition is over it is raised to the boiling temperature. Then a little more concentrated nitric acid is added, and this is persisted in as long as there is a disengagement of red fumes. When the liquid has cooled there will be deposited a great quantity of yellow-coloured semitransparent crystals; and supposing the process properly conducted, neither resin nor artificial tannin makes its appearance. Wash these crystals in cold water, and dissolve them in boiling water, and crystallize a second time. To obtain the carbazotic acid quite pure dissolve these crystals again in boiling water, and saturate them with carbonate of potash. On cooling carbazotate of potash crystallizes. It is best to dissolve these crystals again in water, and to crystallize them two or three times successively. When the carbazotate of potash is sufficiently pure, dissolve it in water and decompose it by nitric, muriatic, or sulphuric acid. When the solution cools beautiful crystals of carbazotic acid are deposited in plates. A good deal of the same acid may be obtained from the mother leys by a similar process. Four parts of indigo yield about one part of carbazotic acid.

<sup>\*</sup> Unverdorben, Poggendorf's Annalen, xi. 393.

<sup>†</sup> Jour. de Phys. Mars. 1788. † Phil. Mag. xxiii. 256.

<sup>§</sup> Ann. de Chim. lxxii. 117. Ann. de Chim. et de Phys. xxxv. 72. ¶ Kohlenstickstoffsaure.

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Properties.

Carbazotic acid thus obtained is crystallized in fine plates, having a silky lustre and a fine yellow colour. It reddens vegetable blues, and has an exceedingly bitter taste. When heated it melts, and is volatilized without decomposition. When suddenly heated it takes fire and burns with a yellow flame, leaving a residue of charcoal. It is little soluble in cold, but very soluble in hot water, and the solution has a deeper yellow colour than the solid acid itself.' It is soluble also in alcohol and ether.

It is not acted on by chlorine or iodine. Sulphuric acid has no action on it cold; when hot it dissolves it; but lets it fall unaltered as it cools. Boiling muriatic acid has no action on it whatever, and aqua regia scarcely alters it. These facts are sufficient to show that it contains no nitric acid, as Chevreul supposed that it did.

It is rather a powerful acid, uniting with and neutralizing the different bases. The carbazotates have the curious property of detonating when heated, as was long ago discovered by Fourcroy and Vauquelin.

Atomic weight. Liebig examined a good many of the carbazotates, and subjected carbazotate of potash and of barytes to analysis. The following were the results which he obtained:

1. Carbazotate of potash.

Carbazotic acid . . . 30·41 Barytes . . . 9·5

The mean of these two analyses gives us 30.71 for the atomic weight of this acid. It was analyzed by Liebig by means of oxide of copper, and found composed of

 Carbon
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The hydrogen, supposing it to contain that principle, scarcely exceeded 1 per cent. of the weight of the acid.

The number of atoms corresponding with this analysis is

 10 atoms carbon
 .
 .
 .
 7.5

 2 atoms azote
 .
 .
 3.5

 12 atoms oxygen
 .
 .
 12.0

But this would make the atomic weight only 23, which does not agree with that deduced from the analysis of the carbazotates. To make them agree we must suppose

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0			,
12 <sub>1</sub> atoms carbon	•	•	9.375
$2\frac{1}{4}$ atoms azote	•	•	4.375
16 atoms oxygen	•	•	16.
			29.750

29.75 approaches nearest to 30.41, the atomic weight deduced from the analysis of carbazotate of barytes.

But Dr. Buff, who has published several interesting papers on indigo, assures us that Liebig ascertained that carbazotic acid is a compound of

16 atoms carbon	•	•	7.5
4 atoms azote	•	•	7.0
10 atoms oxygen	•	•	10.0
			24.5*

But where this determination appeared I do not know. It is equally inconsistent with Liebig's analysis of the carbazotates, and of carbazotic acid.†

#### SECTION XLIII.—OF INDIGOTIC ACID.

The existence of this acid was first pointed out by Chevreul History. in his paper on the action of nitric acid on indigo; but for the first account of its nature and properties we are indebted to Dr. Buff.‡ Fourcroy and Vauquelin had indeed observed it, but they mistook it for benzoic acid. The method of preparing the indigotic acid is as follows:

Very dilute nitricacid is raised to the boiling point, and indigo in fine powder added by little and little. A considerable frothing takes place, the colour of the indigo is immediately destroyed. Indigo is to be added as long as the effervescence continues, taking care to prevent the concentration of the acid, by adding every now and then a little boiling water. The gas evolved consisted of equal volumes of carbonic acid and deutoxide of azote. The yellow coloured liquid thus obtained was separated while hot, from the resinous matter which had been deposited.

<sup>\*</sup> Ann. de Chim. et de Phys. xxxix. 296.

<sup>†</sup> Welter's bitter principle obtained by digesting silk in nitric acid, appears from Liebig's experiments to be also carbazotic acid. But silk yields a much smaller quantity of this acid than indigo.

<sup>‡</sup> Ann. de Chim. et de Phys. xxxvii. 160; xxxix. 290; xli. 174.

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On cooling it let fall indigotic acid in very ill formed crystals. The indigotic acid thus obtained being still impure is to be pressed between folds of blotting paper, to free it from nitric acid as completely as possible, and then dried on the water bath. Hot water now dissolves indigotic acid, and leaves a quantity of insoluble matter behind. The aqueous solution (which is very dilute) is to be mixed with recently precipitated carbonate of lead suspended in water, taking care to stop when the effervescence (at first strong) begins to diminish, and the liquid ceases to be transparent. Unless this precaution be attefided to, much of the acid precipitates in the state of disindigotate of lead. The liquid is now left till the impurities fall to the bottom. The transparent liquid being drawn off consists of a solution of pure indigotate of lead. The lead being separated by sulphuric acid, and the solution concentrated, yields crystals of pure indigotic acid.

Properties.

The crystals are snow white, very bulky while moist, but they diminish very much in volume, and lose their crystalline appearance when dried. The lustre is that of silk, and the colour exceedingly white. The indigotic acid has a weak, acidulous, and bitter taste. It slightly reddens infusion of litmus. 1000 parts of cold water dissolve only one part of this acid; but boiling water dissolves it in any proportion whatever. The solution is colourless. It is volatile. When heated in a glass tube it melts and sublimes without decomposition, giving out a sharp acid smell. On cooling it crystallizes in six-sided prisms. When heated over an open flame it takes fire and burns with a strong flame and the evolution of much smoke.

When digested in concentrated nitric acid it is converted into carbazotic acid. Dilute muriatic and sulphuric acids have no action on it; but when heated in concentrated sulphuric acid a brown coloured solution is obtained, from which water throws down brown flocks. It is not decomposed by chlorine, nor altered. Nascent hydrogen is absorbed by it, and it assumes a copper-red colour, and bluish-red flocks are gradually thrown down. Indigotic acid gives a blood-red colour to the solution of peroxide of iron.

In order to determine the atomic weight of this acid, M. Buff analyzed five different combinations of it with oxide of lead; but the results varied so much that there could be no doubt that every one of the salts examined contained a mixture of some of the others. The two that seemed to be the purest were obtained the first, by dissolving a little carbonate of lead

in a great deal of indigotic acid, and setting the solution aside. Semitransparent yellow needles were deposited, which were freed from all adhering indigotic acid, by digesting them in alcohol. These crystals are soluble in water, but are decomposed at the same time. They are anhydrous, and composed of

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Atomic weight.

The other salt was obtained by pouring a solution of nitrate of lead into indigotate of potash, raised to a boiling temperature. The liquid remained for some time transparent, but fine deep yellow needles gradually fell, which were insoluble in water. They were composed of

Indigotic acid . . . 27.08 Oxide of lead . . . 28

If we consider this last salt as a bi-indigotate of lead, and take the mean of the results, we obtain 26.89 for the atomic weight of indigotic acid.

But the analysis of indigotate of potash, a salt in which no foreign substance existed, gave for the atomic weight of this acid 35.22. For it was composed of

Indigotic acid . . . . . . . . . . . . . . . . . 6

While the analysis of indigotate of mercury gave 35.5 for the atomic weight of this acid.

M. Buff analyzed the acid by means of oxide of copper, and composition. obtained the following constituents:

Azote	•	•	7.55
Carbon	•	•	48.21
Oxygen	•	•	44.24

100.00

The atomic proportions which suit these numbers are the following:

$1\frac{1}{2}$	atom azote	• .	•	2.625
22	atoms carbon	•		16.5
15	atoms oxygen	•	•	15

34.125

This is less than the number derived from the indigotate of potash. If we were to admit the presence of 2 atoms of azote in order to get rid of the half atom, the atomic weight would come out 35, which I think likely to be the true number.

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SECTION XLIV. -- OF URIC ACID.

History.

Various attempts were made by chemists to ascertain the nature of the calculous concretions which occasionally form in the kidneys and bladder, and produce one of the most painful diseases to which we are liable. These attempts were attended with very little success, till Scheele published a set of experiments on the subject in 1776. He examined several of these urinary calculi, and found them composed chiefly of a peculiar acid, the properties of which he described. His results were soon after confirmed by Bergman, who had engaged in a similar set of experiments about the same time.\* 'To the acid thus discovered, Morveau gave at first the name of bezoardic, which was afterwards changed into lithic by the French chemists, when they contrived the new chemical nomenclature in 1787. last term, in consequence chiefly of the observations and objections of Dr. Pearson, was afterwards laid aside, and the name uric acid substituted in its place.

Scheele ascertained that uric acid exists always in human Experiments on the urinary calculi were published by Mr. Higgins in 1789,† and by Dr. Austin in 1791; but little was added to our knowledge of uric acid till Dr. Wollaston published his admirable paper on the calculous concretions in Dr. Pearson published a copious set of experiments on the same subject in 1798, in which he enumerates his trials on uric acid, and endeavours to prove that it is not entitled to the name of acid, but ought to be classed among animal oxides. This drew the attention of Fourcroy and Vauquelin to the subject: they published an excellent treatise on urinary calculi, in which they demonstrate that it possesses the properties of an acid, and confirm the observations of Bergman and Scheele. But for the most complete account of uric acid we are indebted to Dr. Henry, who made it the subject of his thesis published in 1807, and afterwards inserted a paper on it in the second volume of the new series of Manchester Memoirs.

To obtain pure uric acid, Dr. Henry dissolved pulverized calculi (previously known to be composed chiefly of that acid) in a ley of potash, and precipitated the uric acid by means of muriatic or acetic acids. The powder thus obtained was 1rst washed with a little ammonia, to remove any adhering

<sup>\*</sup> Scheele, i. 199 and 210. French Trans.

<sup>†</sup> Comparative view of the phlogistic and antiphlogistic theories, p. 283.

foreign acid, and then edulcorated with a sufficient quantity of warm water.

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I obtained it in considerable quantity from the fæces of the boa constrictor. This serpent voids its excrements about once a month. They are white and solid, and have a certain resemblance to the album græcum voided by dogs. It was digested in caustic potash by which almost the whole of it was dissolved. The solution was drawn off clear from the undissolved sediment, and mixed with a sufficient quantity of pure acetic acid to saturate the whole of the potash. A copious white precipitate fell, which being thoroughly washed with water, and dried in a gentle heat, was pure uric acid.

It was sometimes in the state of a white impalpable powder, Properties. sometimes in small four-sided prisms, having considerable lustre. It is tasteless, very white, very light, and insoluble both in water and alcohol. In concentrated sulphuric acid it speedily assumes the form of a jelly, and upon applying a gentle heat a complete solution is obtained, without altering the colour or transparency of the acid. In nitric acid, even though dilute, it dissolves with effervescence, and when the solution is evaporated to dryness, it assumes a fine pink colour, which becomes much deeper when water is added, so as to have a near resemblance to carmine. In this state it stains wood, the skin, &c. of a beautiful red colour. The watery solution of this matter loses its red colour in a few hours, and it cannot afterwards be restored.\* When the solution of uric acid in nitric acid is boiled, a quantity of azotic gas, carbonic acid gas, and of prussic acid, is disengaged. + Dr. Pearson, by repeated distillations, converted the residue into nitrate of ammonia. When chloring gas is made to pass into water containing this acid suspended in it, the acid assumes a gelatinous appearance, then dissolves; carbonic acid gas is emitted, and the solution yields by evaporation muriate of ammonia, binoxalate of ammonia, muriatic acid, and malic acid.t

It combines with the different bases, and forms a genus of salts called *urates*, for the examination of which we are chiefly indebted to Dr. Henry.

When digested with water holding carbonate of soda in solution, it gradually dissolves, while the carbonic acid is disengaged. The solution, how much soever of the acid is added, still con-

<sup>\*</sup> Scheele, Bergman, Pearson, and Henry.

<sup>†</sup> Fourcroy; Ann. de Chim. xxvii. 267.

<sup>‡</sup> Brugnatelli; Ann. de Chim. xxvii. 267. Fourcroy, x. 222.

tinues to communicate a violet colour to cudbear paper. When Chap. I. the alkali is saturated, a considerable portion of the urate of soda (but not the whole) falls down in the state of a white tasteless powder.

The crystals of uric acid are composed of

1 atom uric acid 2 atoms water	•	•	9 2·25

I found by combining this acid with soda, that its atomic weight is 9! that of the crystals is 11.25. Dr. Prout analyzed the crystals by means of oxide of copper, and obtained for the constituents

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Com	I XUSI	LI(	ou.

6 atoms carbon	•	•	4.5
2 atoms azote .	•	•	3.5
3 atoms oxygen	•	•	3.0
2 atoms hydrogen	•	•	0.25

But we have seen that 2.25 of this weight may be driven off in the state of water, without altering the nature of the acid. Hence the constituents of the anhydrous acid must be

6 atoms carbon	•	•	4.5
2 atoms azote	•	•	3.5
1 atom oxygen	•	•	1
			Ω

Thus it would appear to contain no hydrogen, but to consist of a compound of carbon, azote, and oxygen. The quantity of oxygen which it contains is small, compared with its atomic weight. It is obvious that when ammonia is formed by the action of nitric acid on uric acid, water must be decomposed as well as the acid.

#### SECTION XLV. -- OF PYRURIC ACID.

History,

Scheele observed that when unic acid is subjected to distillation a yellowish white sublimate is obtained, which he considered as analogous to succinic acid. Dr. Pearson, who observed it afterwards, considered it as approaching more nearly to benzoic Dr. Henry first examined it, and showed that it was a peculiar acid, united to ammonia. He determined several of the properties of this acid, but did not distinguish it by an appropriate name. In 1820 it was more particularly studied

by MM. Chevalier and Lassaigne, who gave it the name of pyro-uric acid, and who not only determined its characters in detail, but combined it with bases, and ascertained the nature of its salts.\*

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When uric acid (or calculi of uric acid, or urate of ammonia) is distilled in a retort, hydrocyanate of ammonia is disengaged in the first place, then a thick empyreumatic liquid passes over, which speedily becomes solid; after this the upper part of the retort becomes studded with beautiful and brilliant white plates which preserve that colour if removed immediately, but are sullied and at last dissolved if the distillation be continued. These crystals are pyrurate of ammonia. The liquid and solid matter in the receiver contains also a quantity of the same This salt being dissolved in water and mixed with a solution of diacetate of lead, a white precipitate fell. This precipitate was washed with boiling water, then mixed with water, and a current of sulphuretted hydrogen gas passed through the mixture to precipitate the lead. The liquid thus freed from lead being filtered and concentrated, pyro-uric acid separated in crystals.

Pyro-uric acid is white, and crystallized in small needles. It properties feels somewhat gritty between the teeth. When passed through a red-hot glass tube, it is decomposed into charcoal, oil, carburetted hydrogen, and carbonate of ammonia. Cold water dissolves about the 40th part of its weight of this acid. The solution reddens litmus paper. Boiling alcohol of the specific gravity 0.837 dissolves it, but when the solution cools the acid falls down in small white grains.

Concentrated nitric acid dissolves it, but by evaporation we obtain it again unaltered. It forms soluble salts with most of the bases. Solutions of peroxide of iron, oxide of copper, oxide of silver and of mercury, and of diacetate of lead, are the only substances which occasion precipitates when dropped into pyro-urate of potash. The pyro-urate of peroxide of iron is buff-coloured, that of copper bluish white. The other precipitates are perfectly white.

Chevallier and Lassaigne analyzed the dipyrurate of lead, and found it a compound of

Now 28 represents the weight of two atoms of oxide of lead,

<sup>\*</sup> Ann de Chim. et de Phys. xiii. 155.

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and 11.16 should be the atomic weight of pyro-uric acid. They subjected the pyro-uric acid itself to an analysis by means of oxide of copper, and obtained the following for its constituents:

Composition.

Oxygen	•	•	•	44.32
Carbon		•	•	28.29
Azote .	•	•	•	16.84
Hydrogen	•	•	•	10.00

99.45

As the results only are given, without any details, we have no means of forming an opinion of the accuracy of these analytical experiments. But the number of atoms of each constituent that agrees best with these results, and with the atomic weight of the acid, deduced from the analysis of the pyro-urate of lead, is the following:

5 atoms of oxygen	•	•	5
4 atoms of carbon	•	•	3
1 atom azote	•	•	1.75
9 atoms hydrogen	•	•	1.125

10.875

The atomic weight thus deduced is 10.875, while that from the dipyro-urate of lead is 11.16; the difference is very little more than an atom of water, which might perhaps remain in the salt after it had been made as dry as possible by exposure to heat. Were we to admit 10 atoms of hydrogen instead of 9, the atomic weight of the acid would be exactly 11.

The very great quantity of oxygen and hydrogen contained in this acid, compared with uric acid, is astonishing, and renders it highly worth the attention of themists to resume the analytical investigation of these two acids, in order, if possible, to attain still greater accuracy in our results.

#### SECTION XLVI. OF ASPARTIC ACID.

History.

This acid was discovered, and its properties investigated, by M. Plisson in 1829.\* He obtained it by mixing acetate of lead with the juice of the shoots of asparagus; a white insoluble salt fell, which being washed, mixed with water, and decomposed by a current of sulphuretted hydrogen gas, left aspartic acid in solution in the water. By evaporating this water the aspartic acid was obtained in a solid state.

<sup>\*</sup> Ann. de Chim. et de Phys. xl. 209.

It is a brilliant white powder, which, when viewed through a microscope, appears to consist of four-sided prisms, terminated by dihedral summits, quite transparent and colourless. It has properties no smell, but a slightly acid taste, which soon passes away, leaving the impression of asparagine. It reddens the infusion of litmus. Its specific gravity is 1.873.

At the temperature of  $47^{\circ}\frac{1}{3}$  it dissolves in 128 times its weight of water. But it is much more soluble in hot water, and accordingly a hot solution crystallizes in cooling. It is insoluble in alcohol of 40 Beaumé (specific gravity 0.817), at the ordinary temperature of the atmosphere.

When heated with 12 times its weight of nitric acid it is not destroyed, at least the greatest part of it still remains unaltered.

Aspartic acid when dissolved in water does not occasion a precipitate when dropped into solutions of muriate of barytes or of lime, or into sulphate of magnesia, of manganese, of zinc, or into the salts of iron, the acetate of lead, the sulphate of copper, corrosive sublimate, nitrate of silver, or into tartar emetic. But it decomposes the carbonates.

From the experiments of Plisson, it appears to have the property of converting starch into sugar when boiled for a long time with an aqueous solution of that principle. Other vegetable acids appear to have the same property. But I think it doubtful whether in these cases the change is not independent of the accompanying acid. At least, I know that the hot infusion of barley gradually becomes sweet and susceptible of the vinous fermentation, without the presence of any acid whatever.

All the aspartates are decomposed by heat. Those containing a mineral alkali give out ammonia and hydrocyanic acid, while a cyanodide is formed. The soluble aspartates have a flavour of beef-tea, which is characteristic. It is obvious from all this, that aspartic acid, like the sinapic, contains azote as one of its constituents. No attempt has been made to analyze this acid, but M. Plisson has made a set of experiments to determine the composition of several aspartates with a view of determining the atomic weight of this acid. It appears to be capable of uniting with bases in two proportions, forming neutral aspartates and diaspartates. The following table exhibits the result of M. Plisson's analyses.

l. Aspa	rtat	e of m	agnes	ia.
Aspartic acid		•	•	11.99
Magnesia	•	•	٠.	2.5

Chap. I.	2. Diaspar	te of magnesia.				
Atomic . weight.	Aspartic acid	<b>—</b>				
	Magnesia .	•		•	5	
	3. Aspartate of barytes.					
	Aspartic acid			•	16.31	
	Barytes	•	•	•	9.5	
	4. Dias	par	tate o	f lime.	1	
	Aspartic acid			•	15.83	
	Time				7	

The numbers after aspartic acid in each of these salts, ought to fepresent the atomic weight of that acid. But these numbers deviate too much from each other to enable us to draw any satisfactory conclusions. The analysis of aspartate of magnesia differs so much from the rest that we must reject it altogether. The mean of the other three gives us 16.47. We may therefore assume 16.5 as constituting an approximation to the atomic weight of aspartic acid, though perhaps not a very near one.

#### SECTION XLVII. -- OF NITRO-SACCHARIC ACID.

History.

This acid was discovered in 1820 by M. Braconnot. The process which he followed in order to obtain it is as follows:

12 grammes ( $185\frac{1}{3}$  grains) of strong glue were mixed with twice their weight of strong sulphuric acid. No action took place in 24 hours. Six cubic inches of water were added, and the whole was boiled for five hours, taking care to add water in proportion as it evaporated. The acid was now saturated with chalk, and the whole thrown on the filter. The filtered liquid being concentrated furnished a syrup, which, left for about a month to spontaneous evaporation, yielded granular crystals adhering strongly to the bottom of the vessel. These crystals had a decidedly sweet taste. Being washed with weak alcohol, again dissolved in water and crystallized a second time, they were tolerably pure.

Sugar of glue.

Sugar of glue thus obtained crystallizes with great facility. When the hot solution of it in water is concentrated and set aside a crust forms on the surface, and when this is broken another soon succeeds it. When left to spontaneous crystallization it forms hard crystalline grains, feeling between the teeth like sugar candy, and having the shape of flat prisms or tables. Its taste is as sweet as that of sugar of grapes. It is about as soluble in water as sugar of milk. The solution, though mixed with yeast, does not ferment. Alcohol does not

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dissolve it even when assisted by heat, and though it be weakened by the addition of water. It is not so easily melted nor so easily decomposed by heat as common sugar. When distilled it yields a white sublimate and an ammoniacal liquid, showing that azote exists in it as a constituent. When heated with nitric acid it forms no mucic acid. But another acid is formed to which Braconnot has given the name of nitrosaccharic.

When nitric acid is poured upon sugar of glue no solution takes place, but the sugar becomes perfectly white in consequence of the solution or decomposition of the colouring matter. When the mixture is heated solution takes place, but there is no effervescence takes place, nor any disengagement of red vapours. The evaporation being continued (taking care not to apply too strong heat) till the whole is sufficiently concentrated, it becomes solid on cooling, having the appearance of a crystalline mass. This mass was cleaned by pressure between the folds of blotting paper, and crystallized anew. In this state it constitutes nitro-saccharic acid, the weight of which exceeds considerably the whole weight of the sugar of glue employed.

It is very soluble in water, and readily crystallizes in fine Properties. transparent, flat, striated prisms, similar in appearance to the crystals of glauber salt. Its taste is acid and slightly sweet, very similar to that of tartaric acid. When heated it swells very much, melts and gives out an acid vapour. It produces no change in metallic or earthy solutions. It combines in two proportions with potash, forming a neutral and a binitro-saccharate, both of which crystallize in fine needles. Its taste is nitrous with an impression of sweetness. When thrown upon burning coals it detonates like nitre. The nitro-saccharate of lime crystallizes in beautiful needles. It is not deliquescent and is scarcely soluble in alcohol. Thrown upon burning coals it melts in its water of crystallization, and then detonates like nitre.

With oxide of copper this acid forms a crystallizable salt not altered by exposure to the air; with magnesia an uncrystallizable deliquescent salt; with oxide of lead it forms an uncrystallizable salt not altered by exposure, and resembling gum in appearance. This salt detonates feebly when heated. Nitrosaccharic acid dissolves iron and zinc, with the disengagement of hydrogen gas, and forms with them salts which do not crystallize

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These facts (which are all that have hitherto been determined) leave no doubt that nitro-saccharic acid is a combination of nitric acid and sugar of glue. It is a remarkable circumstance that bases have no disposition to separate the nitric acid from the sugar, but that they combine with both at once. This is a sufficient proof that the sugar of glue does not unite with nitric acid as a base, but so as to form a new compound acid.

It would have been interesting to have known the atomic weight of this acid, and likewise the proportion in which the nitric acid and sugar of glue unite. But no attempts seem to have been made by Braconnot to determine the composition of any of its salts.\*

#### SECTION XLVIII. -- OF NITROLEUCIC ACID.

This acid, which has hitherto been but very imperfectly examined, was discovered by Braconnot about the same time with the nitro-saccharic acid. It was obtained by the following process:

Formation.

A piece of muscle of beef as lean as possible, was well divided and steeped in water till every thing soluble in that liquid was taken up. It was then subjected to pretty strong pressure in a linen cloth. 30 grammes (4631 grains) of this fibrin being mixed with their own weight of concentrated sulphuric acid, softened and dissolved without the acid becoming coloured or the disengagement of any sulphurous acid. It was heated to render the solution more complete, and allowed to cool that a crust of tallow which had appeared might be separated. The solution was then diluted with about six cubic inches of water, and boiled for nine hours, renewing the water from time to time as it evaporated. The acid was then saturated with chalk, and the liquid being separated by the filter and evaporated, yielded an extract not in the least sweet, but having a very marked flavour of roasted meat. When boiled repeatedly in alcohol of the specific gravity 0.847, the alcoholic liquids on cooling deposited about 15 grains of a white matter, which Braconnot distinguished by the name of leucine.

Leucine.

Leucine when dried is a white powder—but it still retains a little animal matter separable by tannin. To free it from this matter the leucine was dissolved in water, and a little tannin cautiously added. After some hours the liquid was filtered

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and then evaporated till a pellicle formed on its surface. This pellicle being removed after 24 hours, small white grains were found at the bottom of the vessel. This was pure leucine. When leucine dissolved in hot water is left for spontaneous evaporation the leucine forms on the surface small round circles like buttons, having a depression in the centre. Leucine has an agreeable taste of boiled meat or soup. It is lighter than water. When heated it melts at a temperature much higher than that of boiling water, emitting the smell of roasted meat, and partly subliming in small white opaque crystals. The liquid which comes over contains empyreumatic oil and ammonia.

Leucine dissolves readily in nitric acid. If we heat the solution to drive off the excess of nitric acid, we observe scarcely any effervescence and no emission of red vapour. The residue evaporated in the sand-bath in a gentle heat assumes the form of a solid crystalline mass, which being dried between folds of bloating paper and redissolved in water, crystallizes in fine divergent needles. These needles constitute nitroleucic acid.

This acid forms with the salifiable bases salts quite differ- Nitro-leucic ent from the nitro-saccharates. Nitroleucate of lime is a salt not altered by exposure to the air, and which crystallizes in small groups. When thrown on burning coals it melts in its water of crystallization, but not so readily as nitro-saccharate of lime. Nitroleucate of magnesia crystallizes and is not altered by exposure to the air. The remaining properties of this acid are still unknown. It is obviously a combination of nitric acid with leucine, and therefore analogous to nitrosaccharic acid in its nature.\*

#### SECTION XLIX .-- OF PURPURIC ACID.

This acid was discovered by Dr. Prout, in the year 1818, History. while engaged in examining the pink-coloured substance formed by heating a solution of uric acid in nitric acid. mode of obtaining the acid was as follows:

He digested pure uric acid-In dilute nitric acid. An effervescence took place, and the acid was dissolved. The excess of nitric acid was neutralized by ammonia, and the evaporation continued. The colour of the liquid became gradually of a deeper purple and dark red granular crystals (sometimes of a greenish hue externally), soon began to separate in abundance.

<sup>\*</sup> Ann. de Chim. ct de Phys. xiii. 118.

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These crystals were composed of purpuric acid and ammonia; they were dissolved in a solution of caustic potash, and heat applied to the solution till the red colour entirely disappeared. The alkaline solution was then gradually dropped into dilute sulphuric acid, which uniting with the potash, left the acid principle in a state of purity.\*

Properties.

Purpuric acid thus obtained is a cream-coloured powder, which, when examined with a magnificr, especially in water, appears to possess a pearly lustre. It has no smell nor taste. Its specific gravity is considerably above that of water, though from its minute state of division it usually takes a considerable time to subside in that fluid.

It is very little soluble in water; 10,000 parts of that liquid not being capable of dissolving one part of the acid. In alcohol and ether it is quite insoluble. It dissolves readily in the concentrated mineral acids and in the alkaline solutions; but it is insoluble, or nearly so, in dilute sulphuric, muriatic, and phosphoric acids, and also in solutions of oxalic, tartaric, and citric acids. Concentrated nitric acid dissolves it readily with effervescence, and purpurate of ammonia is obtained. Chlorine likewise dissolves it, and produces a similar change on it. It dissolves also when assisted by heat in concentrated acctic acid.

It does not sensibly alter the colour of litmus paper. When exposed to the air it does not deliquesce. But it becomes gradually red, and some purpurate of ammonia seems to be formed in it.

When heated it neither melts nor sublimes, but acquires a purple hue from the formation of ammonia, and afterwards burns gradually without yielding any remarkable odour. When distilled it yields a good deal of carbonate of ammonia, some prussic acid, and a little fluid having an oily appearance, while a pulverulent charcoal remains.

It combines with bases, and forms salts to which the name of purpurates has been given. The greater number of these purpurates have a red colour, though some of them are green and some of them yellow. Purpuritacid is capable of decomposing the carbonates when assisted by heat, and it does not, as far is known, combine with any other acid.

Dr. Prout made some trials to determine the composition of this acid by heating it with peroxide of copper. The result of his experiments gave the constituents as follows:

2 atoms hydrogen	•	•	=0.25	Class I.
2 atoms carbon	•	•	= 1.50	Div. II.
l atom azote	•	•	= 1.75	Composition,
2 atoms oxygen	•	•	= 2.00	
			<b>5·5</b> 0	

According to this analysis the equivalent number for purpuric acid is 5.5 or a multiple of it.\*

It may be requisite to state that the attempts which I made to procure this acid by the process of Dr. Prout did not succeed, nor did the phenomena which I observed exactly agree with those described by Vauquelin, who considers the colouring matter and the acid as two different substances. Lassaigne conceives that he has verified this opinion of Vauquelin by decomposing the purpurate of ammonia by means of the galvanic battery. He got a colourless acid collected round the positive pole, while the alkaline substance round the negative pole was deeper coloured than ever.† I suspect that these discordancies are connected with some diversity in the properties of the calculi from which the uric acid was obtained by the different experimenters.

## Erythric Acid.

This acid was formed by Brugnatelli. His method was to dissolve uric acid in a slight excess of nitric acid, to evaporate slowly, and then put the solution by to crystallize in a cool place. These crystals became slowly purple when exposed to the air. The purple colour appears more rapidly if they be dissolved in water and a few drops of ammonia added. The nature of these crystals has not yet been satisfactorily explained. It would seem to be a salt, but what the constituents of this salt are I do not know. I have never had an opportunity of seeing Brugnatelli's paper, which puts it out of my power to enter into farther particulars respecting erythric acid. This name was given from the Greek word equiples, red, in consequence of the red colour which it assumes when exposed to the air.

#### SECTION L .-- OF ALLANTOIC ACID.

This is the name which M. Lassaigne has given to the acid History. discovered by Vauquelin and Buniva in the liquor amnii of the

<sup>\*</sup> Prout, Phil. Trans. 1818, p. 420. † Ann. de Chim. et de Phys. xxii. 334.

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cow.\* Lassaigne examined the liquor contained in the allantois, and likewise that contained in the amnios of the cow, three several times in succession, and always found the acid in question in the liquor contained in the allantois, and never in the liquor amnii of the cow. He is of opinion that the liquid of the allantois had been given to Vauquelin and Buniva instead of the liquor of the amnios, and on that account changed the name from amniotic to allantoic acid.+

Properties.

Allantoic acid is obtained by evaporating the liquid of the allantois. It crystallizes in square prisms, its colour is white, and its lustre pearly. It is insipid, and not altered by exposure to the air. When heated it does not melt but blackens, is decomposed, and yields a great deal of carbonate of ammonia, some hydrocyanate of ammonia, and an oil, and it leaves a light charcoal, which burns away without leaving any residue. Water at the ordinary temperature of the atmosphere dissolves  $\frac{1}{100}$ th part of its weight, and boiling water  $\frac{1}{30}$ th of its weight of this acid. The solution reddens litmus paper; on cooling almost all the allantoic acid precipitates in fine needles.

It dissolves in boiling alcohol, but a portion crystallizes as the solution cools. The aqueous solution of this acid neither precipitates the solutions of lime, barytes, strontian, nor nitrate of silver, nitrate of mercury, acetate nor diacetate of lead. When treated with boiling nitric acid it is converted into a yellow gummy mass, which has an acid taste, but not the least bitterness.

All the allantates are soluble in water and crystallizable. Allantate of barytes crystallizes in white prisms. Its taste is acid, and it is more soluble than allentate of potash. Its constituents, as determined by the analysis of Lassaigne, are

Allantoic acid . . . 63.0 Barytes . . . 9.5

This would make the atomic weight of this acid 63.

The allantate of lead was found composed of

This would make the atomic weight of this acid 58.33. The mean of these two results gives 60.66 for the atomic weight of this acid.

Lassaigne subjected allantoic acid to analysis by means of oxide of copper, and obtained

<sup>\*</sup> Ann. de Chim. xxxiii. 279. † Ann. de Chim. et de Phys. xvii. 295.

Oxygen	•	•	•	32.00	Class I.
Carbon .	•	•	•	28.15	Div. II.
Azote .		•	•	25.24	
Hydrogen	•	•	•	14.50	
all of the second of the secon					
* . <del>_</del>				99.89	

The atomic numbers agreeing with this analysis, and approach- composition. ing nearest to the atomic weight deduced from the salts analyzed, are the following:

• 20 atoms oxygen	•	•	20
23 atoms carbon	•	•	17.25
9 atoms azote	•	•	15.75
72 atoms hydrogen	•	•	9
•			
			60.00

This is of consequence the most complex acid which has hitherto been subjected to analysis.

# SECTION LI.-OF HYDRO-CARBO-SULPHURIC ACID.

Some steps towards the formation of this acid were made by History. Berzelius in his paper on bisulphuret of carbon, but it is to M. Zeise of Copenhagen that we are indebted for a full investigation of its nature.\*

When an aqueous solution of ammonia and bisulphuret of carbon are left for a considerable time in contact with each other in a close vessel, a dark brownish-red liquid is formed, consisting of a mixture of hydro-carbo-sulphate of ammonia and sulpho-cyanate of ammonia, but containing no carbonate of Bisulphuret of carbon dissolves very readily in an alcoholic solution of ammonia. The solution continues alkaline though a considerable excess of bisulphuret of carbon be It becomes speedily yellow, then brown, and smells of sulphuretted hydrogen. In about half an hour yellow feathershaped crystals of hydro-carbo-sulphate of ammonia are formed. These crystals are to be separated and dried by pressure between folds of blotting paper. Being now dissolved in water, and the solution mixed with dilute muriatic acid, an oily liquid separates, which is hydro-carbo-sulphuric acid. This acid is separated from the watery portion by means of a funnel.

Hydro-carbo-sulphuric acid obtained by this process is a properties. reddish brown transparent oily-looking liquid, heavier than

<sup>\*</sup> Schweigger's Jahrbuch, xi. 98, and 170.

water, and having a peculiar smell mixed with that of sulphuretted hydrogen. M. Zeise is of opinion that this acid is a compound of hydrogen with a combination of sulphur and carbon in different proportions from what constitutes bisulphuret of carbon. To this compound he has given the name of xanthine, and he considers it as a compound of

3 atoms sulphur . . 6
1 atom carbon . . . 0.75
6.75

Its catomic weight therefore is 6.75, and it is in reality a tersulphate of carbon if Zeise's notion respecting its constitution be correct. This xanthine has the property of combining with the different bases in the same way as chlorine, bromine, iodine, and cyanogen, and to these compounds, several of which have been described by Zeise, he has given the name of xanthides.

Composition.

Hydro-carbo-sulphuric acid, or hydro-xanthic acid, as it is also called, is a compound, according to Zeise, of

 1 atom xanthine
 .
 .
 6.75

 1 atom hydrogen
 .
 .
 0.125

6.875

Hence the reason of the name. Or we may consider it as a compound of

1 atom bisulphuret of carbon . 4.75 1 atom sulphuretted hydrogen . 2.125

6.875

It is obvious that the atomic constitution of the acid, whichever view we take, will be the same. The first is conformable to the opinions formed by Zeise, but some of the changes which the acid undergoes rather favour the second. Nor are we to consider the constituents of the acid as perfectly established. For Zeise rather drew his deductions from theoretical views than from actual experiment. The salts which this acid forms, and several of which have been examined by Zeise, are called hydro-carbo-sulphates, or hydro-xanthates.

## SECTION LII. -- OF SULPHO-VINIC ACID.

History. • It has been known for many years that when concentrated sulphuric acid and alcohol are mixed together in a retort, the mixture is accompanied by the evolution of much heat, and that when it is distilled a very volatile and inflammable liquid

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is obtained, distinguished by the name of sulphuric ether. Fourcroy and Vauquelin, in a paper on etherification, published in an early volume of the Annales de Chimie, endeavoured to prove that the sulphuric acid merely acted by abstracting a portion of the water, and that ether is alcohol deprived of a certain proportion of its water. This opinion was called in question by M. Dabit,\* who endeavoured to prove that during the process the sulphuric acid undergoes decomposition. that it yields a portion of its oxygen to the alcohol, and that a new acid is formed, intermediate between sulphurous and sulphuric acid. Fourcroy and Vauquelin objected to this opinion of Dabit, that it was altogether unsupported by experiment, and could not therefore be adopted by chemists. † Two years after, Dabit published a second memoir on the formation of ether, t in which he demonstrates by very decisive experiments that a new acid is formed during the conversion of alcohol into ether, by the action of sulphuric acid. It is difficult to explain why no notice whatever was taken of this interesting paper of Dabit, and why no person thought it worth his while to repeat his experiments. The fact is, that ever since chemistry existed as a science, there has always been some individual, whose opinions for the time were adopted by the chemists on the continent without discussion or hesitation. Fourcroy at that time enjoyed that situation in France, and the experiments of Dabit were neglected and forgotten, because they were inconsistent with the opinions of that eloquent lecturer. Dabit prepared several salts containing his new acid as a constituent, and showed by the most decisive experiments that this new acid was neither sulphuric nor sulphurous, though it contained sulphur as an essential constituent.

In the year 1818 Dr. Serturner of Einbeck, published an elaborate paper on the combination of acids with bases and in different substances.§ In this paper he affirms that sulphuric acid in acting on alcohol to form ether, produces no fewer than three acids, which he distinguishes by the names of acidum protænothionicum, acidum deutænothionicum, and acidum tritænothionicum. The first of these acids is obtained, he says, when equal weights of very strong alcohol and sulphuric acid are mixed together. This mixture is to be heated and then mixed with a sufficient quantity of chalk to saturate the acid which it

<sup>\*</sup> Ann. de Chim. xxxiv. 289. † Ibid. xliii. 101.

<sup>†</sup> Ibid. p. 318.

<sup>§</sup> Gilbert's Annalen, lx. 33.

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contains. The liquid being filtered and evaporated yields protoenothionate of lime, from which the acid may be obtained by means of sulphuric acid. The second acid is obtained from the residue after the distillation of ether, by exactly a similar process; and the third acid is formed when the second acid is exposed to the air. It absorbs oxygen, and is converted into tritoenothionic acid.

Next year M. Vogel of Munich published a paper on the action of sulphuric acid on alcohol, with a demonstration of the formation of a new acid, to which he gave the name of sulpho-This paper of Vogel was commented on at considerable length by Serturner, soon after its appearance.+ mixed together equal parts of alcohol of the specific gravity 0.817 and concentrated sulphuric acid, and preserved the mixture for eight days in a stoppered bottle. He then divided the liquid into two equal parts, one of which was saturated with carbonate of barytes, and the other with carbonate of lead. The solutions being filtered and evaporated, yielded crystals of sulpho-vinate of barytes and sulpho-vinate of lead. He separated the sulpho-vinic acid from both of these salts, ascertained its characters, and determined the nature and properties of the sulpho-vinates. He pointed out the analogy between sulphovinic acid and hyposulphuric acid. But he did not subject any of the sulpho-vinates to an analysis.

Soon after the appearance of Vogel's paper, an interesting account of the discovery of sulpho-vinic acid was published by Gay-Lussac, accompanied by some experiments of his own, from which he drew as a conclusion, that sulpho-vinic acid is hyposulphuric acid united with a certain quantity of vegetable matter.‡

In the year 1826, a very interesting set of experiments by Mr. Hennell was published on the mutual action of sulphuric acid and alcohol, with observations on the composition and properties of the resulting compound. In this paper, Mr. Hennell shows the nature of oil of wine, a liquid which is obtained in the process for making sulphuric ether. It is obtained by continuing the distillation after all ether ceases to come off. Mr. Hennell discovered that this oil of wine is a compound of

<sup>\*</sup> Gilbert's Annalen, lxiii. 81. † Ibid. lxiv. 67.

<sup>‡</sup> Ann. de Chim. et de Phys. xiii. 62.

<sup>§</sup> Phil. Trans. 1826, p. 240.

2 atoms sulphuric acid	•	10
4 atoms carbon .	•	3
4 atoms hydrogen .	•	0.5
		12.5

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But always containing in solution less or more of a substance composed of equal atoms of carbon and hydrogen, and which separated sometimes in crystals and sometimes in a liquid state. He found farther that oil of wine has the property of combining with bases and forming neutral salts with them; and these salts being examined were found to possess exactly the character of the sulpho-vinates as described by Vogel. He found also that sulphuric acid, which in some of Mr. Faraday's experiments had absorbed about 80 times its volume of olefiant gas, had by this process been partly converted into sulpho-vinic Mr. Hennell has published a subsequent paper on the action of sulphuric acid on alcohol, but as it relates rather to the theory of etherification than to sulpho-vinic acid, the facts which it contains will come under our review in a subsequent part of this volume when treating of sulphuric ether.

Sulpho-vinic acid may be obtained from sulpho-vinate of lead or sulpho-vinate of barytes. The sulpho-vinate of lead may be decomposed by a current of sulphuretted hydrogen gas, and the sulpho-vinate of barytes by means of sulphuric acid.

The sulpho-vinic acid thus disengaged may be concentrated Properties. by placing it in an exhausted receiver over a basin containing By this process it may be rendered nearly as sulphuric acid. oily-looking as sulphuric acid, and its specific gravity may be raised as high as 1.319. If we attempt to carry the concentration farther the acid undergoes decomposition, sulphurous acid is disengaged, and sulphuric acid remains mixed with a little etherial oil. It undergoes decomposition also if we raise it to the boiling temperature. When of the specific gravity 1.319 it may be left in contact with cold nitric acid without being decomposed, but when heat is applied, deutoxide of azote is disengaged, and sulphuric atid remains. The same alteration is produced when the sulpho-vinates are treated with nitric acid.

This acid cannot be preserved for any length of time without being altered. After a short time it occasions a precipitate in salts of barytes, though at first no such precipitates appear. All the sulpho-vinates hitherto observed are soluble in water. Most of them crystallize and have a sweetish taste, and their

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solutions are not precipitated by the salts of barytes or of lead. They may be exposed for a long time to the air without undergoing decomposition. But when heated they are destroyed, and converted either into sulphates or bisulphates, according to the nature of the salt and the quantity of heat applied.

M. Gay-Lussac showed that sulpho-vinic acid, when decomposed by means of nitric acid, yields twice as much sulphuric acid as remains when a sulpho-vinate is exposed to a red heat. Hence he concluded that the sulpho-vinic acid was the hyposulphuric mixed with some vegetable matter. But Mr. Hennell has shown by direct experiment that this acid is a compound of

Composition.

2 atoms sulphuric acid	•	10
4 atoms carbon .		3
4 atoms hydrogen .	•	0.5
		19.5

so that an atom of it weighs 13.5. It saturates just as much of the bases as half the sulphuric acid which it contains would On that account, Mr. Hennell conceives that one-half of the acid in it is saturated with the carbo-hydrogen, and that only the other half is at liberty to combine with bases. this view of the subject is scarcely compatible with the fact that sweet oil of wine is perfectly neutral, unless it be rendered so by the excess of carbo-hydrogen which it contains. hydrogen contained in sulpho-vinic acid is a compound of 4 atoms carbon and 4 atoms hydrogen. It is therefore analogous to the tetarto-carbo-hydrogen described in the first volume of this work (p. 200), though, as it may be obtained even in a solid state, it is certainly not identical with it. It would appear from this, that carbon and hydrogen are not only capable of forming a variety of compounds by grouping together a greater or smaller number of particles of carbo-hydrogen, as has been explained in a former part of this work (Vol. I. p. 191), but even when the number of atoms is the same, the nature of the compound may be altered by a different mode of arranging We may then consider sulpho-vinic acid as a comthe atoms. pound of

2 atoms sulphuric acid . . . 10
1 atom tetarto-carbo-hydrogen . . 3.5

13.5

It is clear that both the atoms of sulphuric acid are in combina-

tion with the atom of tetarto-carbo-hydrogen, otherwise the barytes salts would undoubtedly act upon it and throw down that portion which is not in combination.

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## SECTION LIII .-- OF XANTHIC ACID.

This acid was also discovered by M. Zeise. His method History. was as follows: To a solution of potash in alcohol bisulphuret of carbon was gradually added till the alkali was neutralized. By this process xanthic acid was formed, which being combined with the alkali constituted xanthate of potash. This salt crystallizes in needles; it is colourless and possessed of considerable brilliancy. When exposed to the air it becomes slightly yellow. Its taste is cooling, sulphureous, and sharp. It is very soluble in water, and yet does not absorb moisture from the atmosphere. It dissolves also in alcohol, and is very slightly soluble in ether.

When muriatic acid or sulphuric acid, in a concentrated state, is poured upon this salt no effervescence takes place, but if these acids be diluted with four or five times their weight of water, a liquid separates heavier than water, and having an exact resemblance to an oil. This liquid is *xanthic acid*.

This acid is transparent and colourless. It is liquid at the Properties. ordinary temperature of the atmosphere, and even when cooled much lower. It is heavier than water, and does not unite with that liquid. When exposed to the air it is soon covered with a white opaque crust. It undergoes spontaneous decomposition when kept under water. Its smell is strong and peculiar, bearing some analogy to that of sulphurous acid. Its taste is acid; it then gives an astringent and bitter impression. It reddens paper stained blue with litmus, and the reddened part soon becomes yellowish-white.

This acid dissolves readily in an aqueous solution of potash, barytes, or ammonia. It disengages carbonic acid from carbonate of potash, and forms xanthate of potash. The other alkaline xanthates may also be made by digesting it on the respective carbonates.

In the open air this acid tatches fire from the flame of a candle, and burns with a strong odour of sulphurous acid. When heated in a retort it undergoes decomposition at a temperature much lower than that of boiling water. Common bisulphuret of carbon is formed and an inflammable gas evolved, which has neither the smell of onions nor of sulphurous acid. It readily dissolves iodine. The solution is at first yellow and then becomes brown. But the colour soon disappears, and in

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two or three minutes (provided too much iodine has not been added) it assumes the form of an oily opaque liquid, having a light yellow colour. The aqueous liquid above this oily matter contains a solution of hydriodic acid.\*

Xanthic acid is characterized by precipitating the salts of copper yellow.

Composition.

According to Zeise this acid is a compound of

4 atoms carbon	. •	•	3
4 atoms sulphur	•		8
3 atoms hydrogen	. •	•	0.375
l atom oxygen	•	•	1
			12:375

This would make the atomic weight 12.375. But this opinion is not founded upon any analysis of the xanthates, but upon the supposition that the acid is a compound of two atoms bisulphuret of carbon, and one atom of alcohol. For alcohol, as we shall find afterwards, is a compound of 1 atom oxygen, 2 atoms carbon, and 3 atoms hydrogen, so that its atomic weight is 2.875; while that of bisulphuret of carbon is 4.75. Thus we have

2 atoms bisulph:	uret	of car	bon	•	•	9.5
1 atom alcohol	•	•	•		•	2.875

12.375

But this opinion, not being supported by satisfactory analyses, cannot be viewed in any other light than an ingenious conjecture. At least in none of Zeise's papers on the subject, which I have had an opportunity of seeing, is the statement supported by experimental evidence.†

Xanthic oil,

During the distillation of xanthate of potash, a substance comes over which Zeise has distinguished by the name of xanthic oil. It is limpid, has a yellow colour, and a very strong and peculiar smell which adheres long to every substance impregnated with it. Its taste is sweet and sharp. Water dissolves

<sup>\*</sup> Zeise; Ann. de Chim. et de l'hys. xxi. 160.

<sup>†</sup> The reader will find the composition of this acid stated on Zeise's authority in L. Gmelin's Handbuch der Theoretischen Chemie, i. 328; but not supported by experimental proof, as Gmelin is always in the habit of giving when any exists. I am induced from this to suspect that the statement is founded on experiment, though I know of none. As I have not had an opportunity of seeing all the periodical works on chemistry in Germany, some of Zeise's papers might have been overlooked by me. But this is not likely to be the case with a professor of chemistry in a German university.

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it in very small quantity. But it is abundantly dissolved in even very weak alcohol. It has no acid qualities, does not precipitate metallic solutions, burns with a blue flame, and the evolution of much sulphurous acid mixed with carbonic acid.

When the xanthates are distilled they are decomposed, sulphuretted hydrogen, carbonic acid, and xanthic oil being formed, and there remains in the retort a sulphuret mixed with charcoal. Nitric acid and chlorifie decompose these salts by destroying the xanthic acid; while diluted muriatic and sulphuric acid decompose them, expelling the xanthic acid. The alkaline xanthates are soluble in water, and they give with salts of lead a white, and with sais of copper a yellow, precipitate. With salts of protoxide of mercury and oxide of silver they give brown and black precipitates, or at least they speedily assume these colours.

#### SECTION LIV. --- OF SULPHO-NAPHTHALIC ACID.

This acid was discovered by Mr. Faraday in the year 1826, History. and described by him in a paper inserted in the Philosophical Transactions for that year. When concentrated sulphuric acid is left in contact with pure naphthaline, a combination gradually takes place, and if the proportion of naphthaline employed be not too great, a complete solution is obtained when the liquid is diluted with water. When carbonate of barytes is digested with this liquid the uncombined sulphuric acid is converted into sulphate of barytes, while a neutral solution of sulpho-naphthalate of barytes is obtained. By filtering the liquid and evaporating, the sulpho-naphthalate of barytes may be obtained in imperfect crystals. By dissolving this salt in water, and exactly saturating the barytes in it with sulphuric acid, and then filtering, the sulpho-naphthalic acid is obtained pure in a state of solution.

This liquid strongly reddens litmus paper, and has a bitter Properties. and acid taste. When strongly concentrated by heat it assumes a brown colour, and on cooling becomes thick and ultimately solid, and is very deliquescent. The heat being renewed it again melted, began to smoke and was charred, but did not flame. It ultimately gave sulphuric and sulphurous acid vapours, and left charcoal.

Another portion of the same aqueous solution of sulphonaphthalic acid was placed over sulphuric acid in an exhausted receiver. In some hours it became by concentration a soft white solid, apparently dry, and after a longer period it was hard and brittle. In this state it was deliquescent in the air; but in close vessels it underwent no change in several months.

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Its taste was bitter and acid, accompanied by an impression of something metallic like that of salts of copper. When heated in a glass tube it melted before it was heated to 212°, and on cooling crystallized from central points; but the whole ultimately became solid. When more highly heated water was first given off, and the acid assumed a slight red tint, but no sulphurous acid was yet driven off, or charring produced, and when tested by muriate of barytes it gave but very slight traces of sulphuric acid. In this state it seems to have been anhydrous. A higher temperature caused a little naphthaline to rise, the red lightid became deep brown, and then asudden action commenced at the bottom of the tube, which spread over the whole, and the acid became black and opaque. When the heat was continued naphthaline, sulphurous acid, and charcoal, were evolved; but a portion of sulpho-naphthalic acid remained undecomposed unless the temperature was raised to redness.

Sulpho-naphthalic acid combines with and neutralizes the different bases, and all the salts of it hitherto formed are soluble in water. When strongly heated they burn with a dense white flame, leaving a sulphate or bisulphate according to the nature of the base.

Composition.

To determine the nature of this acid Mr. Faraday subjected sulpho-naphthalate of barytes to analysis, and obtained from 100 parts of the salt

Barytes .	•		27.57
Sulphuric acid	•	•	30.17
Carbon .	•	•	41.90
Hydrogen .	•	•	2.877

102.517

So that there was an excess of 2.517 per cent. The reason was, that the analysis being made upon only a few grains, any error committed was multiplied many times when it was reduced to 100 grains. But if we consider the salt as a compound of

Barytes	•	•	•	•	27.57  or  9.5
Sulpho-naphth	alic	acid	•	•	72·43 or 24·54

it is obvious that the atomic weight of the acid must be 24.5.

Mr. Faraday considers the constituents of the acid to be

<b>2</b>	atoms	sulphuric	acid	•	•	10
20	atoms	carbon	•	•	•	15
8	atoms	hydrogen		•		1

But it is clear that 2 atoms sulphuric acid	•	•	10 .	Class I., Div. II.
18 atoms carbon .	•	•	13·5	
8 atoms hydrogen .	•	•		
			24.5	

are the proportions which correspond with the atomic weight of the acid as deduced from the analysis of sulpho-naphthalate of barytes. The exact results of the analysis are

2.13 atoms sulphuric acid,

19.75 atoms carbon,

~ 8.13 atoms hydrogen.

Were we to consider sulpho-naphthalic acid as a compound of 2 atoms sulphuric acid and 1 atom of naphthaline, and were we to admit naphthaline to be a compound of

18 atoms carbon	•	•	13.5
9 atoms hydrogen	•	•	1.125
			14.695

which accords with some of the analyses of it that have been made, the atomic weight of sulpho-naphthalic acid would be 24.625. I am inclined to the opinion that this is its true constitution. It resembles sulpho-vinic acid in containing two atoms of sulphuric acid, so that the saturating power of this acid is reduced to one half when it combines with naphthaline. A more detailed examination of this acid will probably throw new light upon the constitution and atomic weight of naphthaline. On this account it seems entitled to more attention than has been hitherto paid to it; for I am not aware that Mr. Faraday's experiments have been repeated. I indeed prepared one or two of the salts which he described, merely to judge of their appearance; but did not subject them to any additional examination.

#### SECTION LV. -- OF VEGETO-SULPHURIC ACID.

This acid, which is obviously analogous to the two preceding, History. was discovered by Braconnot in 1819, during his researches on the action of concentrated sulphuric acid on vegetable substances.\*

When pieces of linen or hemp cloth are left in contact with concentrated sulphuric acid they speedily lose their texture and

<sup>\*</sup> Ann. de Chim. et de Phys. xii. 172.

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are converted into a pulp. When this pulp is diluted with water the greater portion of the linen dissolves, together with the sulphuric acid, leaving a quantity of black matter which is to be separated. The solution is now to be saturated with carbonate of lead in order to get rid of the sulphuric acid; and the sulphate of lead being separated a current of sulphuretted hydrogen gas is passed through the liquid to throw down the lead which was in solution. The liquid thus freed from lead being concentrated cautiously, leaves a transparent substance resembling very closely gum arabic in its properties.

If this gum be mixed with very dilute sulphuric acid, and boiled for some time, it is converted into two very remarkable substances. By far the greatest part of it assumes the form of a crystallizable sugar; but another portion in which the sulphuric acid that constituted a portion of the gum is wholly concentrated, possesses the characters of an acid, and constitutes the substance to which Braconnot has given the name of vegeto-sulphuric. This acid may be separated from the sugar by digestion in rectified spirits, which dissolve the acid together with a small portion of the sugar. Being evaporated to the consistence of a syrup, it was agitated in a close vessel with ether, which assumed a straw colour, and being evaporated left vegeto-sulphuric acid in a state of purity.

Properties.

This acid is nearly colourless, its taste is very acid, almost caustic, setting the teeth on edge. It is deliquescent and incapable of being crystallized. When exposed to a temperature a little elevated it gradually assumes a brown colour. When exposed to the heat of a water-bath it is decomposed, and becomes black at a temperature rather lower than that of boiling water. When in that state, if we dilute it with water, flocks of vegetable matter, partly charred, are deposited. And when muriate of barytes is dropt into the liquid, a precipitate of sulphate of barytes falls. It is decomposed still more rapidly at a temperature above that of boiling water, and suffocating vapours of sulphurous acid are exhaled.

This acid occasions no precipitate when dropt into metallic solutions; it does not even throw down any thing when mixed with nitrate of barytes or diacetate of lead. It effervesces strongly with the carbonates, and dissolves metallic oxides, forming salts which are incrystallizable, deliquescent, and insoluble in rectified spirits. These vegeto-sulphates when heated are decomposed, sulphurous acid being evolved, and a sulphate mixed with charcoal remaining. It dissolves iron and zinc with

a copious evolution of hydrogen gas. The vegeto-sulphates of barytes and lead are very soluble in water, and have the appearance of gum.

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No attempt has been made to analyze any of the vegeto-sulphates, or to determine the constituents of vegeto-sulphuric acid. It obviously contains sulphuric acid as a constituent, and its analogy with the two preceding acids is so close that there can be little doubt of its being a compound of 2 atoms sulphuric acid and 1 atom of sugar of linen. Farther researches on it would be interesting, because they would be likely to throw light on the atomic weight of linen sugar; from which some conclusions might be drawn respecting the atomic weights of the different species of sugar, respecting which we at present know but little.

# SECTION LVI. -- OF SINAPIC ACID.

This acid was discovered by MM. Henry, junior, and History. Garót, in the expressed oil of the sinapis alba; and as they found that sulphur was one of the constituents of it, they gave it the name of acide sulphosinapique. It appears to exist in various cruciform plants. The method of obtaining this acid is as follows:

Digest the expressed oil of sinapis alba for a couple of weeks in  $1\frac{1}{3}$  its weight of alcohol of the specific gravity at least of 0.827 (but the stronger the better), shaking it frequently during the digestion. Then draw off the alcohol, mix it with a little water, and putting it into a retort distil off the half of the alcohol. When the matter in the retort is allowed to cool a precipitate of fatty matter falls which had been held in solution by the alcohol. Free the liquid from this fatty matter, and leave it to spontaneous evaporation. The sinapic acid falls impure in the form of a granular reddish mass. It contains a fatty matter which is removed by means of ether, with which the impure acid is repeatedly macerated in a close vessel. The first portions of the ether acquire a carmine red colour, from fatty matter dissolved. As soon as ether ceases to act upon the acid it is dissolved in a little water, the solution is filtered and left to spontaneous evaporation, or it may be left in the vacuum of the air-pump over sulphuric acid. The acid shoots into small, glittering, half spherical groups of crystals, or into small stars.

Sinapic acid thus obtained has a light yellowish colour. Its properties, taste is bitter, sharp, and sulphureous. It does not redden

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litmus tincture, but blackens it like a solution of a hypo-sulphate. But it reddens the tincture made from the petals of the mallow. Whether these crystals contain water has not been ascertained. They are soluble in water and alcohol, and slightly soluble in ether. The aqueous solution may be evaporated to dryness, and the acid exposed to a heat of 230° without decomposition. When the dry acid is distilled in a retort it is decomposed. A little of the acid indeed sublimes unaltered, but by far the greatest part is resolved into carbonic acid, sulphuretted hydrogen, and ammonia, and a coal which remains in the retort. Even when the aqueous solution is long boiled the acid is partly decomposed, and sulphuretted hydrogen exhales, which blackens paper dipped in acetate of lead.

Composition.

The composition of this acid is very remarkable, since it contains no fewer than 5 constituents, namely, oxygen, hydrogen, carbon, azote, and sulphur. The proportions of these constituents as determined by Henry and Garot are as follows:

Oxygen .	•	•	11.91
Hydrogen	•	•	8.30
Carbon .	•		49.50
Azote .	•	•	12.96
Sulphur .	•	•	17.33

#### 100

None of the salts which this acid forms having been subjected to analysis, we do not know its atomic weight. But the smallest number of atoms which correspond with the preceding analysis is

$1\frac{1}{2}$	atom	oxygen	•	•	1.5
		hydroge		•	1.125
9	atoms	carbon	•	•	6.75
1	atom	azote	•	•	1.75
1	atom	sulphur	•		2.00

#### 13.125

Hence the atomic weight is either 13.125, or a multiple of that number.

The alkaline and earthy sinapates have a bitter taste. Sinapate of potash and of soda shoot out into small crystals about the size of a millet seed. Sinapate of ammonia forms small translucent crystals, which appear to be octahedrons. Sinapate of barytes forms small needles which effloresce in the air and are very soluble in water. Sinapate of strontian is similar, but

does not crystallize so readily. Sinapate of lime dissolves very readily, and when evaporated forms mamillary concretions.

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Sinapic acid gives a purple red colour to the salts of the peroxide of iron, and by this action a very minute quantity of iron may be detected. By this reaction Henry and Garot discovered the presence of sinapic acid in pepper corns and in the seeds of red cabbage, turnips, and radishes, and in water distilled from pepper. But they found no traces of it in the leaves of cresses and cochlearia.

This acid occasions a precipitate in diacetate of lead, nitrate of mercury, and nitrate of silver; the two latter in curdy concretions, which are separated by boiling, and become black. The sinapate of silver is not soluble in nitric acid. Sinapic acid gives a green colour to a solution of sulphate of copper, and a white precipitate gradually falls.\*

Such are the properties of the compound oxygen acids, so far as the present state of our knowledge enables us to go. It is not unlikely that some of them will hereafter require to have their position altered. For it is more than probable that mellitic acid and croconic acid contains nothing but oxygen and carbon, and that therefore they should be placed along with oxalic acid in the first division of this class. The atomic composition of these three acids is probably as follows:

		Carbon.		Oxygen.				
Oxalic	•	2 at	toms	+	3 atom			
Mellitic		2	•	+	5			
Croconic		5		<u>.</u>	4			

But as the absence of hydrogen in the two last of these acids has not been demonstrated by sufficiently accurate experiments, I think it better for the present to let them retain their place among the compound oxygen acids.

If the analysis of hydro-carbo-sulphuric acid be accurate, it contains no oxygen. Zeise has endeavoured to show that there exists a principle to which he has given the name of xanthine, composed of •

3 atoms sulphur	•	•	6
l atom carbon	•	•	0.78

6.78

<sup>\*</sup> Not having Henry and Garot's paper at hand, I have extracted this Section from Berzelius' Lärbok i Kemien, 4 delen, p. 103, which is a pretty faithful abridgment of the paper in question, so far as my recollection goess

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which is capable like cyanogen of combining with the different acidifiable bases, and converting them into acids. Hydro-car-bo-sulphuric acid he considers as a compound of 1 atom of xan-thine and 1 atom of hydrogen. Should this opinion be confirmed by future experiment, we must add another class of acids under the name of xanthine acids. But as Mr. Zeise's experiments are obviously insufficient to establish his opinions upon a sufficiently firm base, I thought it better in the mean time to place this acid along with the oxygen acids with a compound base, to which it obviously bears a striking analogy.

We have no idea at present in what way the numerous atoms composing these compound acids are arranged. Hence a knowledge of their mere atomic constituents is of little importance, excepting so far as it gives us the atomic weight of each acid, and enables us to form some judgment respecting the comparative simplicity or complex nature of each. The following table exhibits the constitution of the first subdivision of these acids so far as it has been determined:

Carbo-hydrogen acids.

"	mese actus	SU	ıaı	as	16	mas	De	GII	detern	1111	ca.		
						Atom			Atoms of carbon.		Atoms of hydrogen		Total.
	Formic	•				3			2	•	1	•	6
	Acetic	•				3			4	•	<b>2</b>	•	9
	Succinic	•		•		3		•	4		${f 2}$	•	9
	Gallic '	•				3		•	6	•	3		12
	Ulminic			•		16			<b>32</b>		16	•	<b>64</b>
	Benzoic					3		•	15	•	6	•	24
	Citric			•		4			4		<b>2</b>	•	10
	Croconic	•		•		4		•	5		1?	•	10?
	Camphoric			•		$4\frac{1}{2}$		•	11		6		$21\frac{1}{2}$
	Mellitic	•				5			2		03		7?
	Tartaric	•				5			4		2	•	11
	Vinic	•		•		5			4	•	4		13
	Suberic					6			6	•	16	•	28
	Mucic			•		8		•	6	•	4	•	18
	Kinic	•		•		15			9	•	10		34

We see from this table that the smallest number of atoms in any of these acids is in the *formic* which contains only 6 atoms, while the most complex is the *ulmic*, which contains no fewer than 64 atoms. In the *gallic* and ulmic acids the atoms of oxygen and hydrogen are just in the proportion to constitute water. In the formic, acetic, succinic, citric, croconic, mellitic, tartaric, vinic, and mucic, the hydrogen is in too small a ratio to saturate the oxygen. Formic acid might be resolved into an atom of water and an atom of olefiant gas, and citric into two atoms

of water and two atoms of dicarbonic oxide. In benzoic, camphoric, suberic, and kinic, it is in too great a proportion.

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The following table exhibits the constitution of such of the fatty acids as have been analyzed.

			1. Solid	l d	acids.				•	
			Atoms of oxygen.		Atoms of carbon.		Atoms of hydrogen.		Total.	Fatty acids.
Stearic	•		• 2		<b>36</b>	•	34	•	<b>72</b>	
Margaric	•		3		35		32		70	
Capric	•		3		18 .	•	14	•	<b>35</b>	
Ricinic			<b>4</b>		24	•	22	•	<b>50</b>	
Pinic	• .	•	9	•	<b>67</b>	•	64	•	140	
			2. Liqui	id	acids.					
			Atoms of oxygen,		Atoms of carbon.		Atoms of hydrogen.		Total.	
Oleic		•	$2rac{1}{2}$ .		35		30	•	67 <sup>‡</sup>	
Phocenic			3 .	,	10		7	•	20	
Butyric			3.		8		5		16	
Caproic	•	•	3.		12	•	10		<b>25</b>	

The striking difference between these acids and the last set consists in the great number of atoms of carbon and hydrogen, compared to the small number of atoms of oxygen. In no case do we find the number of atoms of carbon and hydrogen equal. But in general the approach to equality is so evident that I am disposed to consider these acids as compounds of oxygen with solid or liquid multiples of carbo-hydrogen, containing many more atoms of carbon and hydrogen than any yet met with by chemists. The atomic weights of the solid acids are in general higher than those of the liquid. Are we to infer from this that the tendency to solidity increases with the number of atoms of carbo-hydrogen that unite into one complex atom?

The following table exhibits the constitution of the acids composed of oxygen, carbon, and azote:

•		-	Atoms of oxygen,	Atoms of carbon.	Atoms of azote.	Total.	Carb <b>az</b> oti <b>c</b> acids.
Carbazotic		4	16 .	$12\frac{1}{2}$ .	$2\frac{1}{a}$ .	31	
Indigotic .		•	15	22 .	$oldsymbol{2}^{oldsymbol{ iny}}$ .	39	
Uric	•	•	1.	6.	2:	9	

In these the atoms of azote are always few, scarcely exceeding 2, while those of oxygen and carbon are numerous, with the exception of uric acid, which is much simpler in its composition than the other two.

The following table shows the constitution of those acids Hydro-carbthat are composed of oxygen, carbon, hydrogen, and azote.

Chap, I,			Atoms of oxygen.	•	Atoms of carbon.	•	Atoms hydrogo	Ato	of	Total.
	Purpuric		2		2		2	1	•	7
	Pyruric	•	5		4		9	1		19
	Allantaia		90		00		70	0		194

The following table shows the atomic constitution of those acids that are composed of oxygen, carbon, hydrogen, and sulphur:

Hydro-carbo-
Hydro-carbo- sulphazote
acids.

•	Atoms of oxygen.	Atoms of carbon,	Atoms of hydrogen.	Atoms of sulphur.	Total.
Hydro-carbo-sulphuri	c 0?	· 1	. 1	. 3 .	<b>5</b> ?
Xanthic	1	4	. 3	. 4 .	12
Sulpho-vinic .	6	4	. 4	. 2 .	16
Sulpho-naphthalic.	6	18	. 8	. 2 .	34

The sulpho-vinic is a compound of two atoms sulphuric acid and two atoms olefiant gas. It is not unlikely that sulpho-naphthalic acid is a compound of two atoms sulphuric acid with one atom of naphthaline. The probability is that the constitution of the other two acids, included in this table, is not accurately made out.

It is very doubtful whether these compounds owe their acid qualities to the oxygen which they contain. Certainly the degree of acidity is not proportional to the proportion of this principle which they contain. There can be no doubt that each acid as a whole possesses electro-negative qualities; but these cannot be ascribed to the oxygen, which in the fatty acids must be completely overpowered by the great number of electro-positive atoms with which it is combined.

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### CHLORINE ACIDS.

I have no doubt that the acids formed by the combinations of chlorine with the acidifiable bases are numerous, and they will probably one day rival the oxygen acids themselves. But they have scarcely yet attracted the attention of chemists. The consequence is, that the facts respecting these acids hitherto ascertained, if we except muriatic acid, which had been known and investigated long before its constitution was suspected, are very few. I shall lay them before the readers of this work in the two following sections.

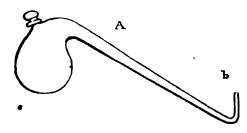
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# SECTION I .-- OF HYDRO-CHLORIC OR MURIATIC ACID.

There is little doubt that this acid was known in the seventh History. century, as it is distinctly alluded to in the writings of Geber. But Glauber seems to have been the chemist who contrived the present mode of obtaining it, by distilling a mixture of sulphuric acid and common salt. It was distinguished by the names of spirit of salt, marine acid, and muriatic\* acid, doubtless because it is obtained from common salt. Mr. Cavendish first obtained this acid in the gaseous state, and mentioned the circumstance in his paper on Factitious Airs, published in 1776;+ but he does not seem to have been aware of the nature of the elastic fluid which he obtained. The subject was afterwards taken up by Dr. Priestley, who ascertained the nature and properties of muriatic acid gas, and must therefore be considered as the true discoverer of it. 1 In 1774 Scheele discovered chlorine gas, and stated the composition of muriatic acid to be chlorine united to phlogiston. By phlogiston he meant hydrogen. Therefore, according to the opinion of Scheele, muriatic acid is a compound of chlorine and hydrogen. This opinion was neglected for many years; but was revived again in 1810 by Sir H. Davy, in consequence chiefly of the experiments of Gay-Lussac and Thenard. The numerous experiments of Davy, assisted by the subsequent discovery of iodine, and its striking analogy to chlorine, gradually established the theory of Davy. I am not aware of any chemist who at present supports the old hypothesis of Berthollet.

Nothing is easier than to procure gaseous muriatic acid in small quantities. We have only to put a little common salt

into the small tubulated retort A, capable of holding three or four cubic inches, and then to pour by the tubular a quantity of sulphuric acid, while the bent extremity of the beak is plunged into a mercurial



trough under the mouth of a small glass jar standing inverted over it and filled with mercury. The gas issues at first rapidly from the beak b. A portion must be allowed to escape before

<sup>\*</sup> Muria is used by Cicero for brine or salt water.

<sup>†</sup> Phil. Trans. vol. lvi. p. 157.

<sup>‡</sup> Pricstley on Air, ii. 276.

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we begin to collect the gas, that we may be sure that all the common air has been driven out of the retort. After a short time the evolution of muriatic acid gas stops. We must then apply the heat of a lamp to the belly of the retort, and the gas will be driven over with such rapidity, that we may in a few minutes fill five or six little jars with it, and thus collect a sufficient quantity to examine its properties.

Properties.

- 1. It is invisible like common air, and capable like it of indefinite contraction and expansion. Its smell is peculiar, and when let into common air it becomes visible by forming a white smeke in consequence of the avidity with which it absorbs moisture. It reddens vegetable blues and has a very sour taste, and possesses powerful corrosive qualities.
- 2. I found its specific gravity at the temperature of 60° and when the barometer stood at 30 inches 1.2843. The true specific gravity has been shown by Gay-Lussac to be the mean of the specific gravity of hydrogen gas and chlorine gas, or 1.2847.
- 3. Animals are incapable of breathing it; and when plunged into jars filled with it, they die instantaneously in convulsions. Neither will any combustible burn in it. It is remarkable, however, that it has a considerable effect upon the flame of combustible bodies; for if a burning taper be plunged into it, the flame, just before it goes out, may be observed to assume a green colour, and the same tinge appears the next time the taper is lighted.\*
- 4. Its refracting power, according to the experiments of Chevreul, is 1.527, that of air being unity.
- 5. Water absorbs this gas with prodigious rapidity. If we fill a phial with it, and take out the stopper while the mouth of the phial is under water, the liquid rushes in with fully as much violence as it would into a vacuum. At the temperature of 69° one cubic inch of water is capable of absorbing 417.822 cubic inches of muriatic acid gas. The temperature of the liquid increases considerably; and its volume at 69° is 1.3438 cubic inch. It is obvious from this that 100 grains of acid of this strength contain 103 cubic inches of the acid gas; and a cubic inch of this acid contains 311.04146 cubic inches of the acid gas. Acid of this strength has a specific gravity of 1.1958, and contains 40.39 per cent. of real acid united with 59.61 of water. In winter liquid acid may be obtained having a specific gravity of 1.212, and probably by artificial cooling the saturation of the

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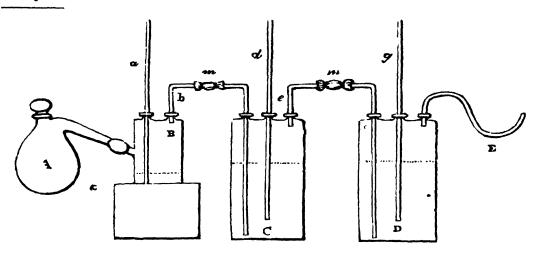
water might be carried still farther. The following table which I constructed with considerable care, from actual experiment,\* exhibits the composition of liquid muriatic acid of various specific gravities.

Atoms acid.	Atoms water.	Acid in 100 of liquid.	Specific gravity
1	-6	40.659	1.203
1	7	37.000	1.179
1	8	33.945	1.162
1	9	• 31.346	1.149
. 1	10	29.134	1.139
1	11	27.206	1.1285
1	12	25.517	1.1197
1	13	24.026	1.1127
1	14	22.700	1.1060
1	15	21.512	1.1008
1	16	20.442	1.0960
1	17	19.474	1.0902
1	18	18.590	1.0860
1	19	17.790	1.0820
1	20	17.051	1.0780

Strength.

Ice also absorbs this gas, and is at the same time liquefied. The quantity of this gas absorbed by water diminishes as the heat of the water increases, and at a boiling heat water will not absorb any of it. When water impregnated with it is heated, the gas is again expelled unaltered. Hence muriatic acid gas may be procured by heating the common muriatic acid of commerce. It was by this process that Dr. Priestley first obtained it.

Liquid muriatic acid, as the solution of the gas in water is Preparation. called, being more employed in chemical experiments than any other acid, requires to be obtained quite free from all impurity; and as the muriatic acid of commerce does not possess that indispensable requisite, it is requisite to prepare it in the laboratory. The apparatus employed for this purpose is represented in the figure in next page. A is a tubulated retort of such a size that a couple of pounds of common salt may be put into it without filling it more than half full. The beak of this retort passes through a perforated cork into the opening of the side of the jar B. This jar has two mouths. Through one of them the tube of safety a passes to the very bottom of the jar. It

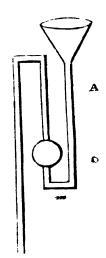


passes through a perforated cork, so as to be air-tight in the mouth of the jar. About an inch of water is put into the jar B, into which the tube of safety a plunges. From the other mouth of the jar B issues the glass tube b, also fixed tight in the jar by means of a perforated cork. This tube bending at right angles passes into one of the three mouths of the tall jar C filled about two-thirds with water. The jar C has three mouths. Into the first passes the glass tube b; into the second the tube of safety d; and into the third the glass tube e. This tube passes to the bottom of another Woolfe's bottle D, which has also its tube of safety g, and the bent tube E, and which like the jar C is filled two-thirds with distilled water. All the mouths of the Woolfe's bottles must be carefully luted with fat lute, and then a piece of cloth dipt into hot glue is to be laid over the joinings and firmly tied on with a string. This, together with the corks, enables the apparatus to withstand the requisite pressure without allowing the gas to escape. The bent tubes b and e would be very apt to break should the apparatus undergo On this account there is a joint in each at m, any agitation. made by having two tubes instead of one, the two extremities of which are brought nearly in contact and tied together by means of a slip of caoutchouc. • I take a ribbon of caoutchouc and dipping it into caoutchouc varnish, make the sides overlap each other, and then tie it in that situation and allow it to dry. It will now form a caoutchouc tube through which the muriatic acid cannot penetrate.\*

<sup>\*</sup> These caoutchouc joints are exceedingly convenient. The thin flat sheets of caoutchouc sold in London answer best. These joints do not answer so

After the apparatus is properly luted, sulphuric acid is to be Class II.

poured by little at a time through the tubular mouth into the retort A.\* This may be either done by simply taking out the stopper and replacing it as quickly as possible after the acid has been poured in. Or we may fix the bent funnel A into the mouth of the retort, making it air tight by passing it through a perforated cork. After the sulphuric acid has passed through this funnel, a portion of it remains at the bending m, which effectually prevents the muriatic gas from escaping that way. advantage of using such a bent funnel is, that we may add sulphuric acid as it is wanted, without deranging the apparatus or stopping



The small quantity of water at the bottom of jar B is first saturated with the gas; then it passes by the tube b into the jar C, and is absorbed by the water in that jar. As the temperature of the water is much raised by this absorption, there is an advantage in surrounding the jar C with cold water, or still better with a mixture of water and ice, when ice can be procured. In proportion as the water absorbs the gas, its bulk increases, and by the time that it is saturated we shall find the jar C nearly filled with liquid muriatic acid. If we continue the process after the water in C is saturated, the gas will pass over into D, and saturate the water which it contains. In this way we may saturate the water in as many Woolfe's bottles as we please, supposing them attached to each other in the way the D is to C.

When the water in C is saturated with muriatic acid gas, its colour is always a light yellow. If we continue the current of gas after the water is saturated, this yellow colour gradually diminishes and at last disappears, or rather the colour is conveyed to the jar D, the water in which in its turn becomes yellow. In this way we may drive the yellow colour from one jar to another as far as we please. The colouring matter, whatever it may be, is very minute in quantity. If we add to well when ammoniacal gas is passed through them. Because caoutchouc absorbs ammonia, and is rendered soft by it, so that it soon gives way.

\* The best proportions are

the process.

7.5 salt, 9.2 sulphuric acid. 1 water.

the coloured liquid a very minute particle of tin, it will be dissolved and the colour disappears. I suspect that the colouring matter is bromine; but I have no other proof except the certainty that bromine exists in minute quantity in common salt, and that a very small portion of bromine is capable of commu-

nicating a similar colour to colourless muriatic acid.

Muriatic acid thus obtained has a strong pungent smell similar to the gas: it emits a white smoke when exposed to the air, which becomes much more conspicuous if a little ammonia be placed in the neighbourhood of the acid.

The following table drawn up by Mr. Dalton gives us the boiling point of this acid at various densities.

Boiling point,

Sp. gravity.			Boiling point.
1.166			170
1.154	•	•	190
1.144	•	•	212
1.136	•		217
1.127	•	•	222
1.121			<b>22</b> 8
1.094	•	•	232
1.075	•	•	228
1.064	•	•	225
1.047	•	•	<b>222</b>
1.035	•	•	219
1.018	•	•	216
1.009	•	•	214
			,ap_148,

We see from this table that the boiling point is a maximum when the liquid is a compound of 1 atom acid and 16 atoms water; or when the liquid contains about  $20\frac{1}{2}$  per cent. of acid. The boiling point of acid of every other strength is lower. Acid containing about 30 per cent. of real acid boils at the same temperature as water. If the acid be stronger its boiling temperature is lower than that of water. The boiling point of acid of 1.203 is 107°.

Composition.

- 6. It has been demonstrated that muriatic acid gas is a compound of equal volumes of hydrogen and chlorine gases, united together without any alteration in bulk.\* Hence its atomic weight is 4.625.
- 7. Mr. Faraday ascertained that muriatic acid gas is condensed into a colourless liquid by a pressure of 40 atmospheres, at the temperature of 50°.+

<sup>\*</sup> See vol. i. p. 107.

Class II.

8. Dr. Henry showed that when electric sparks are passed for some time through muriatic acid gas, it undergoes partial decomposition; a portion of chlorine and hydrogen gases being evolved.\* But this decomposition cannot be carried far, because when hydrogen and chlorine gases are accumulated in any quantity, the electric spark causes them to combine again.

9. When muriatic acid gas and oxygen gas are mixed together and passed through a red-hot porcelain tube, or when electrical discharges are transmitted through such a mixture, water is formed and chlorine gas disengaged. Dr. Henry found that the same decomposition was produced at the temperature of 250° when such a mixture was in contact with a platinum clay ball.+

- 10. When potassium is heated in muriatic gas it liberates one-third of its volume of hydrogen. Davy found that when zinc or tin is heated in this gas they are converted into chlorides, while a quantity of hydrogen gas is disengaged equal to one-half of the muriatic acid gas decomposed. † Charcoal even when ignited to whiteness, produces no change in this gas if it be perfectly dry. Nor is it probable that it would be decomposed by azote, phosphorus, sulphur, or selenium, though I am not aware that the experiment has been tried. It is decomposed by all the metals which decompose water, namely, iron, zinc, tin, and antimony, and also by the metallic oxides. the last case water is formed and a metallic chloride. these oxides consist of those of the more powerful bases, the decomposition is accompanied by the evolution of much heat. Thus if pure anhydrous barytes be put into this gas it becomes chloride of barium with the disengagement of light, while water is condensed on the inside of the jar containing the gas.
- 11. It is at present a subject of discussion among chemists no muriates exist? whether muriatic acid be capable of combining with bases, and forming muriates, or whether at the instant of combination a double decomposition does not take place; the hydrogen of the muriatic acid uniting with the oxygen of the base and forming water, while the chlorine combining with the other constituent of the base produces a chloride. In many cases of combination the phenomena are such that either explanation may be applied; while in others there can be no hesitation in adopting the last explanation as the true one. Thus if we dissolve 13.75 silver in nitric acid, and mix the neutral solution with 7.5 of common salt, we obtain 18.25 of a white matter, which must be chloride of silver. For it contains

Phil. Trans. 1812, p. 240. † Ibid. 1824. 1 Ibid. 1810. H.

Chap, I,

Silver . . . 13.75 Chlorine . . . 4.5

## 18.25

In the same way when 13 lead is dissolved in nitric acid and mixed with the requisite quantity of common salt, we obtain a white matter weighing exactly 17.5, and therefore chloride of lead.

If we dissolve 4.25 zinc in muriatic acid, and evaporate cautiously to dryness, we obtain a white matter weighing 9.875. If we heat this matter to incipient ignition in a glass tube it gives out 1.125 of water, and there remains 8.75 of chloride of zinc. We may therefore consider the white compound either as a compound of

1 atom chloride of zinc	•	•	8.75
1 atom water	•	•	1.125
			9.875
or as a compound of			
I atom muriatic acid	•	•	4.625
I atom oxide of zinc		•	5.25

9.875

The atomic weights and the elements are the same whichever of the two opinions we adopt. The only difference consists in the way in which these atoms are combined. This subject will come under our review more particularly hereafter, when we give an account of the different chlorides or muriates which possess saline properties.

# SECTION II.—OF OTHER CHLORINE ACIDS.

I have no doubt that the number of chlorine acids will very much increase as soon as chemists turn their attention to the subject. But hitherto very few attempts have been made to determine whether those chlorides which contain acidifiable bases be capable of combining with, and neutralizing those chlorides that contain alkalifiable bases.

1. The chlorides of sulphur and phosphorus do not seem possessed of acid properties. At least the attempts which I made to combine them directly with alkaline chlorides did not succeed. It is evident from many chemical phenomena that the chlorides of potassium and sodium are alkaline bodies capable of combining with, and neutralizing various acid chlorides, as

for example the chlorides of gold and platinum. But the chlo- Class III. ride of sulphur is incapable of dissolving these bodies even when assisted by heat. Neither did they dissolve one or two metallic chlorides which I exposed to their action. But no sulphuret was formed when the chloride of sulphur was digested over some metallic chlorides, whose bases have a very strong affinity for sulphur.

- 2. Bonsdorf has shown that corrosive sublimate\* possesses acid properties, and is capable of combining and forming salts with a great variety of alkaline chlorides. This indeed has been long known, though Bonsdorf is the first who has explained the nature of these combinations in a satisfactory manner. I shall describe the new salts which he formed in a subsequent part of this work, when I come to describe the chlorine acid salts.
- 3. There can be little doubt that the chlorides of gold, platinum, palladium, rhodium, iridium, and osmium possess acid properties,+ and that the salts which have been distinguished by the name of double chlorides of gold and sodium or potassium, of platinum and sodium, or potassium and sal ammoniac, &c. are in reality salts formed by the union of a chlorine acid with a chlorine base. These salts, which amount to a considerable number, will be described in a subsequent part of this work, among the chlorine acid salts.
- 4. I have not had time to make any trials with the chlorides of arsenic and antimony; but should not be surprised to find them capable of combining and forming salts with the alkaline chlorides. The subject at any rate requires to be investigated.

## CLASS III.

#### BROMINE ACIDS.

Bromine has been known for so short a time, and is still so scarce and so dear, that we need not be surprised that this class of acids is still almost unknown. In fact there is only one acid belonging to this class which has been hitherto examined. will constitute the subject of the following section.

# SECTION I .-- OF HYDROBROMIC ACID.

This acid was discovered by M. Balard, and to him we are

- \* Ann. de Chim. et de Phys. xxxiv. 142; xliv. 189, 244.
- + See Bonsdorf referred to above.

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indebted for every thing respecting it yet known. I have given a short account of its properties in the first volume of this work (p. 109), and I have nothing farther to add to that description.

It is a compound of one volume of bromine vapour, and one volume of hydrogen gas united together without any alteration in the bulk. Hence its atomic weight is 10·125, and its specific gravity in the gaseous state must be 2·8125. This acid combines with bases, and forms a genus of salts which have been distinguished by the name of hydrobromates. It has not been yet determined whether these salts are really hydrobromates or only bromides, or compounds of bromine with the metallic bases of the alkalies. The difficulty is of the same nature as occurs with regard to the salts formed by means of muriatic acid.

#### CLASS IV.

#### IODINE ACIDS.

The analogy between oxygen, chlorine, bromine, and iodine, is so great that we can scarcely hesitate to admit that iodine, like the other three supporters, has the property of forming acids when it combines with various of the acidifiable bases. But except hydriodic acid, the properties of which have been described in the first volume of this work (p. 110), hardly any of the iodine acids have been hitherto investigated. M. Bonsdorf has shown that the periodide of mercury possesses the characters of an acid, and is capable of combining with and saturating several of the alkaline iodides, as iodide of potassium, of sodium, of zinc, of iron.\* Similar combinations have been made by M. Boullay. There can be no doubt that the number of iodine acids will increase rapidly, now that the attention of chemists is turned to the subject. It is known already that the iodide of arsenic possesses acid properties, and this will probably be the case with the periodide of antimony. would expect also the iodides of the family of noble metals to be acids, as this is the case with their chlorides. It were to be wished, therefore, that some chemist would set about the investigation of their properties, and of the salts which they may be capable of forming.

Class V. Sect. II.

## CLASS V.

#### FLUORINE ACIDS.

I have given in the first volume of this work (page 89), the reasons which have induced chemists to believe that fluoric acid is a compound of fluorine and hydrogen; that fluorine is an electro-negative substance similar in its properties to oxygen, chlorine, bromine, and iodine, and capable like them of combining with the various acidifiable bases, and of converting them into acids. As fluorine has not yet been obtained in a separate state, this opinion cannot be considered as demonstrated, yet the opinion is so plausible and so strongly supported by analogy that it has been very generally adopted.

We are at present acquainted with eight acids, which are considered as combinations of fluorine and an acidifiable basis. These are,

- 1. Hydrofluoric acid,
- 2. Fluoboric,
- 3. Fluosilicic,
- 4. Fluomolybdic,
- 5. Fluotungstic acid,
- 6. Fluochromic,
- 7. Fluocolumbic,
- 8. Fluotitanic.

No combination of fluorine with the nine remaining acidifiable bases has yet been discovered. These eight acids will be described in the following sections.

### SECTION I .- OF HYDROFLUORIC ACID.

This is the acid which has been described in the first volume of this work (p. 87), under the name of fluoric acid. I have already given an account of the process by which it may be procured in a state of purity, and detailed its properties so far as they have been determined. Nothing farther remains but to give an account of the salts which it forms, and which have been examined in detail by Gay-Lussac and Thenard, and by Berzelius. They will occupy our attention in a subsequent part of this volume.

### SECTION II. -- OF FLUOBORIC ACID.

This acid was discovered in 1808 by Gay-Lussac and The-History. nard.\* Its properties and preparation have been already given in Vol. I. p. 218, of this work. It has not yet been analyzed,

<sup>\*</sup> Recherches Physico-chimiques, ii. 37.

but I am disposed, for the reasons assigned (Vol. I. p. 220), to consider it as a compound of

1 atom fluorine . . . 2.25 2 atoms boron . . . 2

4.25

and to consider its atomic weight as 4.25.

Berzelius says that when fluoboric acid gas is absorbed by water, a considerable quantity of boracic acid is deposited. If the liquid acid be cooled or very slowly evaporated, an additional quantity of boracic acid separates; but if it be concentrated at an elevated temperature, it volatilizes without leaving any residue.\* It would appear from this that the hydrofluoric acid formed at first by the decomposition of water is again destroyed, and the original fluoboric acid constituted anew by the action of heat. If these decompositions be accurately stated by Berzelius, they seem to me to demonstrate that the composition of fluoboric acid can be nothing else than

3.25

In order to reconcile this composition with the atomic weight 4.25, can we admit the presence of an atom of oxygen in fluoboric acid?

The fluoborates which have been examined by Berzelius, will be described in a subsequent part of this volume.

# SECTION III. -- OF FLUOSILICIC ACID.

History,

This acid was first obtained in the gaseous state by Priestley, but it was not properly distinguished from hydrofluoric acid before the publication of the experiments of Gay-Lussac and Thenard. I have described the method of procuring it in the first volume of this work (page 229).

Properties,

It is a transparent colourless gas, having a smell very similar to that of muriatic acid, and forming a white smoke when mixed with common air. It is not altered by exposure to a red heat. I found its specific gravity 3.6. When potassium is heated in it combustion takes place, and a chocolate-coloured substance is formed which differs in its nature according to the proportion of potassium employed. Fluoride of potassium is

<sup>\*</sup> Kongl. Vetens. Acad. Handl. 1824, p. 69.

always formed, and a quantity of silicon disengaged, which is commonly united to potassium. Fluosilicic acid gas combines with twice its volume of ammoniacal gas, and forms a volatile salt. This salt is obviously composed of Class V. Sect. III.

If we consider it as neutral (it is the only saline compound of this acid yet formed), it is obvious that the atomic weight of fluosilicic acid is 6.5.

Now if the ratio of its constituents be as I have shown (Vol. I. Composition. p. 229), 1 atom fluorine and 1 atom silicon, it follows either that this acid is a compound of

2 atoms fluorine . . 4.52 atoms silicon . . 2

or that the ammoniacal salt is a bifluosilicate of ammonia. The first of these opinions is by far the most probable.

When fluosilicic acid gas comes in contact with water, it deposites a quantity of silica in a gelatinous state, and by that deposition a quantity of hydrofluoric acid is formed. The silicon decomposes water, and uniting with its oxygen is converted into silica, while the fluorine uniting to the hydrogen of the water becomes hydrofluoric acid. The liquid, supposing it freed from the deposited silica, is, according to the experiments of Berzelius, a compound of

so that it constitutes a compound acid whose atomic weight is Hydrofluo-8.875. This new acid may be distinguished by the name of hydrofluosilicic acid. It combines with the different bases, and forms a genus of salts which may be denominated hydrofluosilicates, and which have been examined by Berzelius. They will come under our review in a subsequent part of this volume.

The method of forming this compound acid in a liquid state is to cause a current of fluosilicic acid gas to pass through a bent glass tube, the extremity of which comes very near, but does not actually touch the surface of the water, to be impregnated with the acid, taking care to agitate the water during the whole proChap. I.

cess, in order to break the crust of silica which speedily forms on its surface. Or we may put about an inch of mercury into the bottom of a glass jar, and after having plunged the beak of the glass tube which conveys the gas under the surface of the mercury, we may pour over it the water to be impregnated. Even in this case the water must be occasionally stirred, otherwise a tube of silica would be formed, through which the gas would escape unaltered. Were we to plunge the end of the tube in the water it would be speedily choked up by the silica deposited in it, and the process would be stopped. When we have sufficiently impregnated the water with the acid we must throw the whole upon a cloth, and after the liquid has passed through we may squeeze the gelatinous silica to remove as much of the liquid as possible, but we must not wash it, because the silica in that state is soluble in water.

The liquid acid thus prepared has an acid taste. If we drop into it any salt having potash, soda, or lithia for a base, a gelatinous precipitate falls, so transparent and colourless, as to be at first invisible. Salts with base of barytes, on the contrary, throw down a white and crystalline precipitate. If we add just the quantity of any base which saturates the compound acid (its atomic weight being 8.875) we form hydrofluosilicates. But if we add a greater quantity of base than is requisite for this purpose, silica is thrown down, and a simple hydrofluate formed. On this account Berzelius considers the acid as a simple mixture of hydrofluoric and fluosilicic acids. But I think it more natural to view it as analogous to hydrosulphuric acid, sulphovinic acid, and sulphonaphthalic acid, in which the atomic weights of the acids, in consequence of their state of combination, is reduced to one-half. I have no doubt that the number of these compound acids will considerably increase hereafter.

## SECTION IV .-- OF FLUOMOLYBDIC ACID.

History.

This acid was first examined by Berzelius.\* It is obtained by dissolving molybdic acid in fluoric acid. This solution is made with great facility. It has an acid, metallic, and disagreeable taste. When evaporated it dries into a yellow syrupy mass, which shows no tendency to crystallize. When heated, its colour becomes bluish. If we dry it we can no longer dissolve it completely in water. Yet it continues a compound of fluoric and molybdic acids.

<sup>\*</sup> Kong. Vetens. Acad. Handl. 1824, p. 325.

This double acid combines with the bases, and forms a set of Class V. salts which may be called fluomolybdates. Only one of these \_ salts has been examined by Berzelius, namely, the fluomolybdate of potash. To obtain it we have only to mix a solution composition. of molybdate of potash with fluoric acid, and evaporate the Crystals of fluomolybdate of potash fall in small The analysis of this salt is attended with considerable difficulty. Berzelius however subjected it to analysis, but his description of the method which he employed is not very intelligible. He seems to have dissolved the salt in water, and to have thrown down the fluoric and molybdic acids by means of acetate of lead. From the residual liquid the lead was thrown down by carbonate of ammonia, and muriatic acid being added and the whole evaporated to dryness and heated, the potash was obtained in the state of chloride of potassium. The precipitate, consisting of molybdate and fluate of lead, was digested in hydrosulphuret of ammonia, by which the molybdenum was dissolved in the state of sulphuret. It was evaporated, and by calcination converted into molybdic acid and weighed. water was determined by heating it along with oxide of lead, and ascertaining the loss of weight. The fluoric acid seems merely to have been inferred from the weight wanting to make up the constituents to the original weight of the salt subjected to analysis. The following table exhibits the result of the analysis of the salt thus managed:

(	9		
Potash .	•	•	31.63
Molybdic acid	•	•	45.80
Fluoric acid	•	•	16.57
Water .	•	•	6.00

100.00

Now the atomic weight of potash is 6, of molybdic acid 9, and of fluoric acid 2.375. Hence these numbers are proportional to

> 1.033 atom potash, atom molybdic acid, 1.366 atom fluoric acid. 1.039 atom water.

Except the fluoric acid, which amounts to 11 atom, it is obvious that each of the other constituents constitute only 1 atom. Now, if we attend to the way in which the fluoric acid was estimated, we must see at once that there is a certainty that it is overrated. For all the loss which must undoubtedly have Chap. I.

been sustained is considered as fluoric acid. Had the loss amounted to 2 per cent. (which is not an excessive allowance) the quantity of fluoric acid would be reduced to 1·19 atom, or less than  $1\frac{1}{5}$  atom. If to this we add that molybdic acid being volatile, there was a considerable chance of some of it being lost during the analysis, which would affect the proportion of all the other constituents, we can scarcely doubt that the true quantity of fluoric acid in the salt is 1 atom.

There is reason then to conclude that fluomolybdic acid is a compound of

1 atom fluoric acid .	•	2.375
1 atom molybdic acid	•	9
		11.975

Its atomic weight is 11.375. So that by the union of these two acids their capacity of sat uration is reduced to one-half. It would appear from this, that fluoric acid resembles sulphuric acid in this curious property. Fluomolybdate of potash is obviously a compound of

1 atom fluomoly	bdic a	cid	11.375
1 atom potash	•	•	6
1 atom water	•	•	1.125
			18.5

## SECTION V. -- OF FLUOTUNGSTIC ACID.

History.

This acid was also first examined by Berzelius.\* It resembles the last, but the constituents seem to be more feebly united. There can be little doubt that it is a compound of 1 atom fluoric acid and 1 atom tungstic acid united together, and capable of saturating no more of a base than either of the constituents would do if it were separate. Or by their union the capacity of saturation of the two acids is reduced to one-half of what it was when they acted separately. The atomic weight of the fluotungstic acid is obtained by adding that of its two constituents together:

1 atom tungstic acid 1 atom fluoric acid	•	•	15·5 2·375
1 atom muoric acia	•	•	
			17.875

It is therefore 17.875.

<sup>\*</sup> Kong. Vetens. Acad. Handl. 1824, p. 320.

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When fluoric acid is poured upon tungstic acid we obtain a yellow milky liquid, which is soluble in a great quantity of water. Calcined tungstic acid is very little soluble in fluoric acid. If we evaporate the solution by a gentle heat we obtain a yellow syrupy mass, which finally cracks, gives out fluoric acid, and assumes a greenish colour. If we pour water on this matter we obtain a milky liquor, and we obtain an acid solution, but the greatest part of the tungstic acid refuses to dissolve. Yet it retains fluoric acid, which it does not give out unless it be strongly calcined in an atmosphere of ammonia. No tungstic acid escapes with the fluoric.

This compound acid combines with different bases, and forms salts which have been called fluotungstates. The only salts of this class hitherto examined are fluotungstate of ammonia and fluotungstate of potash, both of which crystallize in scales similar in appearance to boracic acid. Fluotungstate of potash is easily formed by dissolving tungstate of potash in fluoric acid and evaporating the solution. It is very little soluble in cold water. Boiling water dissolves it better, but on cooling it is mostly deposited again in crystalline scales. Its taste is bitter and slightly metallic. It is not altered by exposure to the air, nor by digesting it in water. According to the analysis of Berzelius, its constituents are

Potash .		24.24
Tungstic acid	•	59.57
Fluoric acid	•	11.39
Water .	•	4.80
		100.00

The fluoric acid was estimated from the loss sustained during composition, the analysis. That loss was considered as fluoric acid. These numbers are equivalent to

1.05 atom potash, 1 atom tungstic acid, 0.87 atom fluoric acid, 1.09 atom water.

It is possible that a little of the fluoric acid may have made its escape with the water, and it is not unlikely that the tungstic acid may have retained a little potash. This analysis, however, leaves little doubt that the true constitution of the salt is

Chap, I.	1 atom fluotungs	17.875		
	l atom potash	•	•	6
	l atom water	•	•	1.125
				<b>25</b>

so that this salt resembles in its composition fluomolybdate of potash, and fluotungstic acid is exactly similar in its nature to fluomolybdic acid.

### SECTION VI. OF FLUOCHROMIC ACID.

History.

This compound was discovered by M. Unverdorben, and described by him in the year 1826.\*

When equal weights of fluor spar and chromate of lead are triturated together and put into a leaden retort with three times their weight of smoking sulphuric acid,+ and then gently heated, a gas is generated, which may be collected in a platinum vessel over mercury. This gas is transparent, and has a light red colour. It cannot be collected in glass vessels, because it is instantly decomposed by the glass, fluosilicic acid being formed, and chromic acid deposited. When ammoniacal gas comes in contact with it combustion ensues, and the two gases explode when mixed in any considerable quantity. heavy, much more so than fluosilicic gas, though from its peculiar properties it has been hitherto impossible to determine its specific gravity with accuracy.

It is not condensed into a liquid when exposed to the temperature of 32°. Water absorbs it, and converts it into fluoric and chromic acids. It is by means of this gas that pure chromic acid is obtained: the process has been described in the first volume of this work (page 335).

Unverdorben analyzed this gas by dissolving it in water and getting rid of the fluoric acid by the addition of silica. chromic acid which remained he converted into protoxide of He has only given us the result of this analysis, Composition. chromium. which, he says, indicates the gas to be a compound of

٠ د

Fluoric acid	•	•	38.13
Chromic acid	•	•	61.87
			100.00

<sup>\*</sup> Poggendorf's Annalen, vii. 318.

<sup>†</sup> Common concentrated sulphuric acid will answer the purpose.

or of

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Fluorine Chromium	•	•	66·6 33·4
			100.0

How the weight of the gas analyzed was determined does not appear; probably by the increase of weight in the water when it was impregnated by the gas. These numbers are proportional to 1.18 atom fluoric acid.

1 atom chromic acid.

Probably, therefore, it consists of an atom of each acid united together, or of an atom of fluorine united to an atom of chromium. The second of these suppositions from the constitution of chloric acid is not so probable as the former. For unless we suppose the gas a compound of  $2\frac{1}{2}$  atoms fluorine and 1 atom chromium, it is impossible that it could be converted by the decomposition of water into chromic acid and fluoric acid. But the analysis of Unverdorben will not accord with such a supposition. The probability then is that this gas is a fluochromic acid and a compound of

1 atom fluoric acid . . . 2·375
1 atom chromic acid . . . 6·5
8·875

No attempt has been made to ascertain whether it be capable of combining with bases, and if so what its atomic weight is.

#### SECTION VII. -- OF FLUOCOLUMBIC ACID.

This acid was first formed and examined by Berzelius, during History. his researches on fluoric acid.\*

When fluoric acid is poured upon columbic acid which had been previously heated to redness, the columbic acid falls to powder, but the fluoric acid dissolves nothing. Yet the columbic acid has combined with a quantity of fluoric acid, which may be afterwards driven off by calcination. Columbic acid prepared by fusion with bisulphate of potash, and then digesting the saline mass in water, dissolves readily in fluoric acid, and forms a limpid and colourless solution. When this solution is left to spontaneous evaporation it becomes concentrated to a certain point, at which it stops. If it be now kept in a heat not exceeding 86°, it becomes still more concentrated, and deposites crystals. By continuing the evaporation the

<sup>\*</sup> Kongl. Vetens. Acad. Handl. 1824, p. 282.

whole is converted into a white enamel-looking mass. The crystals are completely soluble in water. When exposed to a dry atmosphere they effloresce. This compound acid combines with bases, and forms a class of salts which have been called fluocolumbates, several of which have been described by Berzelius; and one of which, the fluocolumbate of potash, he subjected to a careful analysis.

This salt was formed by saturating the hot fluocolumbic acid with potash till a precipitate began to fall. On cooling, the salt was deposited in scales, somewhat similar to boracic acid. These crystals dissolve completely in water, though with some difficulty. The salt dissolves best in hot water, but boiling water decomposes it. It may be obtained also by mixing bifluate of potash with columbic acid and water, and heating the mixture. Berzelius is of opinion that there are two proportions in which this compound acid combines with potash, but this conclusion depends upon theoretical views that are liable, to say the least of them, to great uncertainty.

The following table exhibits the composition of this salt as determined by three different analyses, the mean of which is given:

Potash .		•	<b>23.536</b>
Columbic acid	•	•	56·993
Fluoric acid	•	•	19.470

100.000

The fluoric acid was not obtained, but determined by the loss in the analysis.

Composition.

This analysis does not accord with any atomic proportions whatever. It corresponds with

1.63 atoms potash,

1 atom columbic acid,

3.4 atoms fluoric acid.

The quantity of fluoric acid is so great that it is impossible to believe that all the loss sustained was owing to it. Analogy would lead to the conclusion that fluocolumbic, like the three preceding acids, is a compound of

1 atom columbic acid	•	•	23.75
1 atom fluoric acid	•	•	2.375
			26.125

and that its atomic weight is 26·125. The salt from analogy should be composed of

1 atom fluocolumbic acid 1 atom potash	•	26·125 6	Class V. Sect. VIII.
		32.125	

Subsequent experiments must determine how far these analogies are borne out by facts.

SECTION VIII .-- OF FLUOTITANIC ACID.

This acid also was first examined by Berzelius during his History. researches on fluoric acid.\*

When fluoric acid is poured upon titanic acid heat is evolved, even though the titanic had been previously calcined, and a complete solution is effected by the action of heat. When the solution is evaporated by a gentle heat to the consistence of a syrup it deposites crystals, which do not dissolve completely in water, but are decomposed into two particular combinations, one of which is acid and soluble, while the other has an excess of base and is insoluble. This last combination is decomposed with considerable difficulty by exposure to a red heat in an atmosphere of ammonia. Berzelius considers the acid solution as analogous to liquid hydrofluosilicic acid, that is a compound of hydrofluoric acid and fluotitanic acid. This acid combines with the different bases, and forms a class of salts to which the name of fluotitaniates has been given, and several of which have been examined by Berzelius. He has subjected the fluotitaniate of potash to analysis, in order to enable us to form correct notions respecting the nature of the compound acid which it contains.

This salt is obtained when the acid liquid is saturated with potash till it begins to let fall a precipitate no longer redissolved by agitation. When the solution is concentrated it deposites the salt in brilliant scales like boracic acid. These crystals dissolve in water without decomposition. When heated they give out a little water, which appears to have been only mechanically lodged among the particles of the salt. When distilled in a platinum apparatus, there comes over an acid liquid which contains both fluoric acid and titanic acid. From the experiments of Berzelius it appears that titanic acid and fluoric acid are not capable of forming a gaseous compound. Unverdorben found that when a mixture of rutile, fluor spar, and sulphuric acid, is heated in a glass retort, the gas which comes

<sup>\*</sup> Kongl. Vetens. Acad. Handl. 1824, p. 279.

over contains titanic acid. He considers the gas thus obtained to be a combination of fluoride of silicon and fluoride of titanium. But he could obtain no gaseous fluoride of titanium when the mixture was heated in a leaden apparatus.\*

Berzelius analyzed the fluotitaniate of potash, and obtained

Potash		•		38.7
Titanic acid	•	•	•	35.0
Fluoric acid	•	•	•	26.3
				100.0

Composition. These numbers are proportional to

1 atom potash, 1.03 atom titanic acid, 1.7 atom fluoric acid,

It would appear (if any confidence can be put in this analysis) that the acid consists of

1 atom titanic acid	•	•	$5 \cdot 25$
$1\frac{1}{a}$ atom fluoric acid	•	•	3.5625
			0.0105

Perhaps the half atom may have been in the state of hydro-fluoric acid, simply combined with the fluotitanic acid composed of one atom titanic acid and one atom fluoric acid.

The greater number of the acids belonging to this class are still very imperfectly known. Considerable obscurity still hangs over the combinations of fluoric acid with other acids, which can only be cleared up by farther investigation. The subject is attended with peculiar difficulties, because all the experiments require to be made in platinum or leaden vessels, which prevents us from observing the phenomena so well as when vessels of glass can be employed.

#### CLASS VI.

# CYANOGEN ACIDS.

We are indebted to an accident for the original fact from which the whole of this important branch of chemistry derives its origin.

History.

About the year 1710 Diesbach, a manufacturer of colours in Berlin, wishing to prepare some lake by precipitating a decoc-

<sup>\*</sup> Poggendorf's Annalen, vii. 320.

Class VI.

tion of cochineal, alum, and green vitriol, with potash, borrowed some alkali for that purpose from Dippel. This chemist was the discoverer of a peculiar animal oil which goes by his name. He prepared it from blood; and the alkali with which he furnished Diesbach had been employed in the process. Instead of the red precipitate which he expected, a beautiful blue powder fell to the bottom. On mentioning the circumstance to Dippel, that chemist ascribed the formation of the powder to the action of his alkali on the alum and vitriol. It is not unlikely that he had calcined the potash together with a portion of blood. Be that as it may, he succeeded in discovering a method of procuring the blue powder at pleasure, and it was announced as a pigment in the Berlin Miscellanies for 1710. The preceding history, however, was only communicated to the public by Stahl 20 years after.\*

This powder was called *Prussian blue*; and the method of Formation of Prussian blue. procuring it remained concealed, because it had become a lucrative article of commerce, till Dr. Woodward published a process in the Philosophical Transactions for 1724, which he had procured, as he informs us, from one of his friends in Germany. This method was as follows: Detonate together four ounces of nitre and as much tartar, in order to procure an extemporaneous alkali; then add four ounces of dried bullock's blood; mix the ingredients well together, and put them into a crucible covered with a lid, in which there is a small hole: calcine with a moderate fire till the blood emits no more smoke or flame capable of blackening any white body exposed to it; increase the fire towards the end, so that the whole matter contained in the crucible shall be moderately but sensibly red. In this state throw it into four pounds of water, and boil it for half an hour. Decant off this water, and continue to pour on more till it come off insipid. Add all these liquids together, and boil them down to four pounds. Dissolve an ounce of sulphate of iron in half a pound of water, and eight ounces of alum in four pounds of boiling water: mix all the three solutions together while boiling hot. An effervescence takes place, and a powder is precipitated of a green colour. Separate this precipitate by filtration, and pour muriatic acid upon it till it becomes of a beautiful blue; then wash it with water and dry it.+

<sup>\*</sup> Stahl's Experiments, Observat. Animadvers. ccc. numero. Chim. et Phys. p. 281.

<sup>†</sup> Phil. Trans. xxxiii. 15.

Chap. L

Different explanations were given of the nature of this precipitate by different chemists. Mr. Brown immediately repeated the process of Woodward, ascertained that other animal substances, as beef, may be substituted for blood; that the alum is useful only to dilute the colour; and that the blue pigment is produced by the action of the alkali (altered by blood) on the iron of the vitriol. He ascertained, too, that prussian blue is insoluble in muriatic acid, and that the green colour is owing to a mixture of prussian blue and oxide of iron, and that the muriatic acid developes the blue colour by dissolving the oxide of iron.\*

These facts were of considerable importance; but they threw no light upon the theory of the process. An explanation of this was first attempted by Geoffroy, who had ascertained that any animal body whatever might be substituted for blood. According to him, the blood communicates a portion of inflammable matter, or phlogiston, to the alkali, and this inflammable matter revives the iron of the vitriol and brings it to the metallic state. A greater quantity of blood, by increasing the inflammable matter, will enable the alkali to revive still more of the iron, and thus to strike a blue at once, instead of a green.† Though this explanation was approved of at the time by the best chemists, it was far from satisfactory.‡ Macquer soon after proceeded, by way of experiment, and added a new step to the facts ascertained by Brown.

That celebrated chemist ascertained the following facts:

Experiments of Macquer.

That celebrated chemist ascertained the following facts:

1. When an alkali is added to a solution of iron in an acid, the iron is usually precipitated of a yellow colour, and soluble in acids; but if iron be precipitated from an acid by an alkali prepared by calcination with blood (which has been called a prussian alkali), it is of a green colour.

2. Acids dissolve only a part of this precipitate, and leave behind an insoluble powder which is of an intense blue colour. The green precipitate therefore is composed of two different substances, one of which is prussian blue.

3. The other is an oxide of iron; and the green colour is owing to the mixture of the two substances.

4. When heat is applied to this prussian blue, its blue colour is destroyed, and it becomes exactly similar to common oxide of iron. It is composed therefore of iron and some other substance, which heat has the property of driving off.

5. If it be

<sup>\*</sup> Phil. Trans. 1724, xxxiii. 17.

<sup>†</sup> Lewis's Neuman's Chem. p. 72.

boiled with a pure alkali, it loses its blue colour also, and at Class VI. the same time the alkali acquires the property of precipitating of a blue colour solutions of iron in acids, or it has become precisely the same with the prussian alkali. 6. Prussian blue, therefore, is composed of iron and something which a pure alkali can separate from it, something which has a greater affinity for alkali than for iron. 7. By boiling a quantity of alkali with prussian blue, it may be completely saturated with this something, which may be called colouring matter, and then possesses the properties of a neutral salt. 8. When iron dissolved in an acid is mixed with an alkali saturated with the colouring matter, a double decomposition takes place; the acid unites with the alkali, and the colouring matter with the iron, and forms prussian blue. 9. The reason that, in the common method of preparing prussian blue, a quantity of oxide is precipitated, is, that there is not a sufficient quantity of colouring matter (for the alkali is never saturated with it) to saturate all the iron displaced by the alkali; a part of it therefore is mixed with prussian blue. Muriatic acid dissolves this oxide, carries it off, and leaves the blue in a state of purity.—Such were the conclusions which Macquer drew from his experiments.

The nature of the colouring matter, however, was still un-Macquer supposed it to be phlogiston. According to him, prussian blue is nothing else than iron supersaturated with phlogiston. This overdose protects the iron from acids, and prevents the magnet from acting on it. Heat drives off this dose, and leaves the prussian blue in the state of common iron.\* From this theory, which differed but little from that of Geoffroy, the alkali saturated with the colouring matter of prussian blue received the name of phlogisticated alkali. Macquer having observed that it did not act on alkaline and earthy solutions, while it precipitated all the metals, proposed it as an excellent test for detecting the presence of these last bodies.

The subsequent experiments of chemists threw an air of suspicion on Macquer's theory. Baumé ascertained, that when prussian blue is distilled, it always yields a portion of animal oil; + a product not very likely to appear if the powder contained nothing but phlogiston and iron. Deyeux and Parmentier, Bergman, Erxleben, Delius, and Scopoli, submitted prussian blue to distillation, and obtained a quantity of ammonia. Fontana ascertained that prussian blue detonated with nitre.

<sup>\*</sup> See Macquer's Dictionary, i. 177. + Baumé's Chemistry, ii. 601.

Landriani obtained, by distillation, a little acid liquid and oil, and a great quantity of azotic gas and carburetted hydrogen gas. These facts were still more inconsistent, if possible, with Macquer's theory. Morveau advanced another in 1772; namely, that the phlogisticated alkali, besides phlogiston, contained also an acid which acted the principal part in the phenomena produced.\* Sage affirmed that the colouring matter in phlogisticated alkali was phosphoric acid; but this opinion was refuted by Lavoisier.† Bergman also announced his suspicions that it was an acid, but an unknown one.‡

• Such was the knowledge of chemists respecting the nature of this colouring matter, when Scheele all at once removed the veil, and explained its properties and composition. This he performed in two dissertations on prussian blue, published in

the Stockholm Transactions for 1782 and 1783.6

He observed that the prussian alkali, after being exposed for some time to the air, lost the property of forming prussian blue; the colouring matter must therefore have left it.

Researches of Scheele,

He put a small quantity of it into a large glass globe, corked it up, and kept it some time; but no change was produced either in the air or the prussian alkali. Something must therefore displace the colouring matter when the alkali is exposed to the open air, which is not present in a glass vessel. Was it carbonic acid gas? To ascertain this, he put a quantity of prussian alkali into a glass globe filled with that gas, and in 24 hours the alkali was incapable of producing prussian blue. It is therefore carbonic acid gas which displaces the colouring matter. He repeated this experiment with this difference, that he hung in the globe a bit of paper which had been previously dipped into a solution of sulphate of iron, and on which he had let fall two drops of an alkaline lixivium in order to precipitate This paper was taken out in two hours, and became covered with a fine blue on adding a little muriatic acid. Carbonic acid, then, has the property of separating the colouring matter from alkali without decomposing it.

He found also that other acids produce the same effect. Hence he concluded that the colouring matter might be obtained in a separate state. Accordingly he made a great many attempts to procure it in that state, and at last hit upon the following method:

<sup>\*</sup> Digressions Academiques, p. 249. ‡ Notes on Scheffer, § 165.

Class VI.

Mix together 10 parts of prussian blue in powder, 5 parts of the red oxide of mercury, and 30 parts of water, and boil the mixture for some minutes in a glass vessel. The blue colour disappears, and the mixture becomes yellowish green. upon a filter; and after all the liquid part has passed, pour 10 parts of hot water through the filter to wash the residuum com-The oxide of mercury decomposes prussian blue, separates its colouring matter, and forms with it a salt soluble The liquid therefore which has passed through the filter contains the colouring matter combined with mercury. The other component parts of the prussian blue being insoluble, do not pass through the filter. Pour this mercurial liquid upon 2½ parts of clean iron filings, quite free from rust. same time 1 part of concentrated sulphuric acid, and shake the mixture. The iron filings are dissolved, and the mercury formerly held in solution is precipitated in the metallic state. cause of this sudden change is obvious: The iron deoxidizes the mercury, and is at the same instant dissolved by the sulphuric acid, which has a stronger affinity for it than the colouring matter has. There remains in solution therefore only sulphate of iron and the colouring matter.

Now the colouring matter being volatile, which the sulphate of iron is not, it was easy to obtain it apart by distillation. Accordingly he distilled the mixture in a gentle heat: the colouring matter came over by the time that one-fourth of the liquor had passed into the receiver. It was mixed, however, with a small quantity of sulphuric acid; from which he separated it by distilling a second time over a quantity of carbonate of lime. The sulphuric acid combines with the lime and remains behind, which the colouring matter cannot do, because carbonic acid has a stronger affinity for lime than it has. Thus he obtained the colouring matter in a state of purity.

It remained now to discover its component parts. He formed a very pure prussian blue, which he distilled, and increased the fire till the vessel became red. The small quantity of water which he had put into the receiver contained a portion of the blue colouring matter and of ammonia; and the air of the receiver consisted of azote, carbonic acid gas, and the colouring matter. He concluded from this and other experiments, that the colouring matter is a compound of ammonia and oil. But when he attempted to verify this theory by combining together ammonia and oil, he could not succeed in forming colouring matter. This obliged him to change his opinion; and at last.

he concluded that the colouring matter is a compound of ammonia and charcoal. He mixed together equal quantities of pounded charcoal and potash, put the mixture into a crucible, and kept it red-hot for a quarter of an hour; he then added a quantity of sal ammoniac in small pieces, which he pushed to the bottom of the melted mixture, kept it in the fire for two minutes till it had ceased to give out vapours of ammonia, and then threw it into a quantity of water. The solution possessed all the properties of the prussian alkali. Thus Mr. Scheele succeeded in forming the colouring matter.

• This colouring matter was called prussic acid by Morveau in the first volume of the chemical part of the Encyclopedie Methodique; an appellation which soon became general in Great Britain and France.

Of Berthollet,

These experiments of Scheele were repeated and carried still farther by Berthollet in 1787; who applied to the explanation of the composition of the colouring matter the light which had resulted from his previous experiments on the component parts He ascertained, in the first place, that the phloof ammonia. gisticated alkali is a compound salt, containing prussic acid, the alkali, and oxide of iron; that it may be obtained in octahedral crystals; and that when mixed with sulphuric acid, and exposed to the light, it lets fall a precipitate of prussian blue. next object was to ascertain the component parts of prussic acid. When chlorine is poured into prussic acid, obtained by Scheele's process, the acid becomes more odorous and more volatile, less capable of combining with alkalies, and precipitates iron from its solutions, not blue, but green. He conceived that in this case it had combined with oxygen, acquired new properties, and been converted into a new substance, which he called oxyprussic acid.

From these experiments, and others similar to them, Berthollet concluded, that prussic acid does not contain ammonia ready formed; but that it is a triple compound of carbon, hydrogen, and azote, in proportions which he was not able to ascertain. This conclusion was verified by Mr. Clouet, who found, that when ammoniacal gas is made to pass through a red-hot porcelain tube containing charcoal, a quantity of prussic acid is formed.\* This experiment does not succeed unless a pretty strong heat be applied to the tube.+

In the year 1806, a most valuable paper on prussic acid and

Proust.

<sup>\*</sup> Ann. de Chim. xi. 30.

<sup>†</sup> Jour. de l'Ecole Polytechn. I. iii, 436.

its compounds was published by M. Proust.\* Though he did not succeed in procuring the acid in a separate state, nor in ascertaining its constituents with rigid accuracy; he pointed out a great number of new and important facts which were of much utility, and which facilitated the subsequent investigation of Gay-Lussac. To this last illustrious chemist we are indebted Gay-Lussac, for an easy process for obtaining prussic acid in a state of purity,+ for an accurate description of its properties when thus obtained, and for a rigid determination of its composition and constitution. He showed that it was a combination of hydrogen, with a compound body, to which he gave the name of cyanogen. This body is analogous to the supporters, and capable like them of combining with different bases and converting them into acids.

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Mr. Porrett had previously shown that it was capable of and Porrett. combining with sulphur, and forming a new acid, to which the name of hydro-sulpho-cyanic acid has been since given. And Berthollet had shown that it was also capable of uniting with chlorine, and forming an acid which has got the name of chlorocyanic acid; though the real nature of this acid was first ascertained by Gay-Lussac. || Still considerable obscurity hung about the salt originally formed by Macquer, and called by him phlogisticated potash. It was afterwards denominated prussiate of potash, and its nature and properties were successively investigated by different chemists. But the nature of the precipitates which it forms with metallic salts remained unexamined till Berzelius published a set of experiments on the subject in the year 1819,¶ which settled several points with great accuracy; though there are still some others which admit of more than one explanation.

Some additional facts have been more lately added to this interesting branch of chemical science by Wöhler, Gay-Lussac, Liebig, and Mr. Edmund Davy. I shall endeavour to lay as clear a view as possible of all the different branches of this difficult but interesting subject in the following sections.

#### SECTION I .- OF CYANOGEN.

I have given an account of the method of preparing cyanogen, and described its properties in the first volume of this work (p. 209).

<sup>\*</sup> Ann. de Chim. lx. 185. † Ibid. lxxxiii. 215. ‡ Ibid. xcv. 136.

<sup>§</sup> Phil. Mag. xxxvi. 196. || Ann. de Chim. xcv. 136. || Kong. Vetens. Acad. Handl. 1819, p. 242; and Ann. de Chim. et de Phys. xv. 144.

Chap, I.

It is a compound of two volumes of carbon vapour and one volume of azotic gas united together, and condensed into one volume. Hence we obtain its specific gravity, by adding together twice the specific gravity of carbon vapour, and the specific gravity of azotic gas.

Composition.

Sp. gr. of carbon vapour = 
$$0.4166 \times 2 = 0.8333$$
  
Sp. gr. of azotic gas . . . =  $0.9722$ 

1.8055 =

specific gravity of cyanogen gas. Volumes of carbon and azotic gas bearing the same relation to each other that atoms do, it is obvious that cyanogen is a compound of

2 atoms carbon . . 
$$= 1.5$$
  
1 atom azote . .  $= 1.75$   
 $= 3.25$ 

So that its atomic weight is 3.25. We may obtain the specific gravity of the gas, by multiplying its atomic weight by 0.5555. For  $3.25 \times 0.5555 = 1.8055$  the same as before. Now Gay-Lussac found by experiment 1.8064 which comes within less than  $\frac{1}{2000}$  th part of the theoretic number. The two, therefore, in this case may be considered as identical.

Cyanogen has the property of combining with a great variety of bases, and of forming a set of saline compounds exceedingly analogous to the *chlorides*, and which have received the name of *cyanodides*. The greater number of these compounds possessing the properties of salts, I shall reserve the description of them till I come to the *salts*, which will occupy our attention in a subsequent part of this volume. But there are one or two compounds of a more complicated nature, which may be noticed here.

Action of cyanogen on ammonia. 1. When a current of cyanogen gas is passed through an aqueous solution of ammonia, no fewer than four different compounds are formed. 1. Prussiate of ammonia, or hydrocyanate of ammonia, as it is also called. 2. The dark brown substance described in the first volume of this work (p. 211), as precipitated when a solution of cyanogen in alcohol is set aside. 3. Oxalate of ammonia. 4. A peculiar crystallizable body, resembling cyanodide of ammonia, but certainly a different substance.\* It is probable that the oxalic acid and hydrocyanic acid are produced by the mutual action of the water and cyanogen on each

<sup>\*</sup> Wöhler, Kong. Vetens. Acad. Handl. 1824, p. 328.

other. For four atoms of cyanogen and three atoms of water, might, by mutually decomposing each other, produce one atom \_ of oxalic acid and three atoms of hydrocyanic acid.

3 water contain 4 cyanogen contain	3	+			Azot		Carb.
	3	+	3	+	4	+	8
1 oxalic acid 3 hydrocyanic acid		-		•	0	•	
•	3	+	3	+	3	+	8

There is a surplus of 1 atom of azote, which must either enter as a constituent into the dark brown matter or into the crystallized substance. This crystallized substance may be obtained pure by decomposing cyanodide of lead by caustic ammonia, or cyanodide of silver by sal ammoniac. It has a white colour, crystallizes in needles, and dissolves easily in water and in Its solution is neutral, and it is not precipitated by lead or silver, or by any of the other metallic salts. digested in caustic potash no ammonia is given out. to contain water of crystallization. When heated to redness with potassium abundance of cyanodide of potassium is obtained.

2. If alcohol be saturated with cyanogen gas, and then with of sulphuret. sulphuretted hydrogen gas, it assumes a dark yellow colour, and ted hydrogen and cyanogen. soon after small red crystals are deposited. They have a fine scarlet colour, considerable lustre, and are opaque. They are scarcely soluble in cold water; but they dissolve in hot water, from which, however, they are again deposited as the liquid cools. This substance is but little soluble in alcohol. When gently heated it partly sublimes unaltered, but the greatest part becomes black, while much sulphuretted ammonia is disengaged, and a black coaly matter remains. When passed through hot oxide of copper a great deal of ammonia is disengaged, which does not render lime water muddy, and therefore contains no carbonic acid. Wöhler, to whom we are indebted for all these facts, ascertained by digesting it in aqua regia that it contained 53 per cent. of sulphur. I think it not improbable that these crystals consist of hydrosulphocyanic acid. This acid contains 54.23 per cent. of sulphur, which approaches pretty near the estimate of Wöhler. However, the action of it on the alkalies does not correspond with this notion of its nature.

These red crystals dissolve in sulphuric acid, giving the liquid a yellow colour, and they are again precipitated when the acid is diluted with water. The alkaline carbonates dissolve them with the assistance of heat, and the solution is a mixture of sulphuretted potassium and sulphocyanodide of potassium. They are very soluble in caustic potash. The solution is yellow. When the crystals are mixed with a solution of acetate of lead the acetic acid is immediately disengaged and a fine orange precipitate falls, similar in appearance to chromate of lead. The colour remains after the powder is dried, provided only a very gentle heat be applied. But if it be heated, or even boiled in water, it is converted into sulphuret of lead. If the orange precipitate be digested in caustic potash sulphuret of lead separates, and we obtain a solution of cyanodide of potassium, and sulphocyanodide of potassium. By analyzing this orange powder it was found to contain in one experiment 64 and in another 64.5 per cent. of lead. Now sulphocyanodide of lead is a compound of

> Sulphocyanogen . 7.25 or 35.81 Lead . . . 13 . 64.19

> > 100.00

This approaches so closely to Wöhler's analysis as to render it probable that the orange precipitate is merely a sulphocyano-dide of lead. However, this conclusion is opposed by the different effect which sulphocyanate of potash produces upon the salts of lead.\*

Of persulphuret of potassium and cyanogen.

3. When a current of cyanogen gas is passed through a solution of persulphuret of potassium much sulphur is precipitated, and a quantity of the brown charry matter also makes its appearance, and when the solution is concentrated crystals of sulphocyanodide of potassium are obtained. If this sulphocyanodide be heated to redness in an atmosphere of cyanogen gas, a good deal of sulphur is driven off, and the mass becomes at first black from decomposed cyanogen. But the darkness of the colour speedily diminishes, and the substance becomes at last a colourless fused body, which on cooling becomes a white salt, which proves on examination to be sulphocyanodide of potassium.†

When a current of cyanogen gas is passed through a solution of protosulphuret of potassium, no sulphur is precipitated, and we obtain a mixture of cyanodide of potassium and sulphocy-

\* Kong. Vetens. Acad. Handl. 1824, p. 329. † Ibid. p. 331.

anodide of potassium. The reason is obviously because the Class VI. sulphur present is only capable of converting one-half of the potassium into sulphocyanodide. When cyanogen gas is passed through hydrosulphuret of potash the above described red crystals are obtained, rendering it probable that hydrogen is one of the constituents of this red matter.\*

# SECTION II. -- OF HYDROCYANIC ACID.

The first person who obtained this acid in a separate state was Scheele. He obtained it by the process described in page 213 of this volume. The following is the process recommended by Process of Gay-Lussac. Gay-Lussac. Put into a small tubulated retort a mixture of prussiate of mercury+ and muriatic acid. The quantity of acid should be less than would be requisite to decompose the prussiate of mercury completely. To the beak of the retort fit a glass tube about 2 feet in length and about 6 ths of an inch wide. Fill the first third of this tube with fragments of marble in order to retain any muriatic acid that might come over (but care should be taken to prevent this as much as possible). The remainder of the tube is to be filled with chloride of calcium to retain the water. To the extremity of this tube adapt a small receiver and surround it with ice, or still better, with a mixture of snow and salt. Apply a moderate heat to the retort. The hydrocyanic acid passes over and condenses at first on the marble. But it is easy, by applying a gentle heat, to drive it along the tube, and into the receiver.

The process recommended by Gautier is however easier and of Gautier. cheaper. It is as follows: Fuse the yellow salt well known under the name of ferruginous prussiate of potash, or frequently called simply prussiate of potash, in a vessel to which atmospherical air has not access. This salt is considered at present as a double cyanodide of potassium and iron. By this process the cyanodide of iron is decomposed and an inflammable gas The iron is converted into a carburet, which may comes over. be separated by dissolving the fused salt in water. If we evaporate the filtered solution we obtain a white salt, distinguished by the name of cyanodide of potassium. And that it really

<sup>\*</sup> Kong. Vetens. Acad. Handl. 1824, p. 333.

<sup>†</sup> This salt is obtained by boiling red oxide of mercury and prussian blue together, and evaporating the solution formed till it crystallizes. The crystals constitute prussiate of mercury, or cyanodide of mercury as it is now called.

<sup>‡</sup> Ann. de Chim. p. 144.

contains potassium is obvious from this: If you put a plate of copper into its solution potassium is immediately precipitated; but in consequence of the presence of water in the liquid it is speedily converted into potash with a very evident effervescence. We see from this that copper is capable of throwing down potassium from its combinations.\* Put the cyanodide of potassium thus obtained into a flask or retort slightly moistened with water, and add to it muriatic acid by a little at a time. The hydrocyanic acid is disengaged in a gaseous state. Cause it to pass through a tube filled with fragments of dry chloride of calcium, and receive it into a small flask kept as cool as possible by being surrounded by a mixture of snow and salt. Here the acid condenses into a liquid.

Of Mr. Clarke.

As hydrocyanic acid is very much employed in medicine, and as its efficacy is very much connected with its strength, it comes to be an object of considerable importance to be in possession of a method by which it can be easily prepared by a common apothecary in a state exactly the same in point of strength at The following process, suggested by Mr. Clarke, apothecary to the Glasgow Infirmary, possesses this requisite. In 100 drachms of water dissolve 81 drachms of cyanodide of potassium,  $\dagger$  and add to the solution  $18\frac{3}{3}$  drachms of crystallized tartaric acid previously dissolved in 20 drachms of water. A double decomposition takes place. Bitartrate of potash falls down, and about 120 drachms of water will remain, holding in solution 33 drachms of hydrocyanic acid, or 2.81 per cent. of the solution is hydrocyanic acid. Of acid of this strength 8 drops may be given thrice a day in a glass of water. The only impurity in the acid when thus prepared is a small quantity of cream of tartar, which, in a medical point of view, is of no consequence whatever.

Properties.

Hydrocyanic acid thus prepared is a colourless liquid, having a strong smell similar to that of peach blossoms. Its taste is sharp, and at first appears cooling, but it soon excites a burning sensation in the mouth, and it is very asthenic, and indeed a virulent poison. At the temperature of  $44^{\circ}\frac{1}{2}$  its specific gravity is 0.7058, at the temperature of  $64^{\circ}\frac{1}{2}$  its specific gravity is 0.6969. It boils at the temperature of  $79.7^{\circ}$ , and congeals about the temperature of  $5^{\circ}$ . The cold which it produces when allowed to evaporate in the open air, even at the temperature of  $68^{\circ}$ , is sufficient to congeal it. Its appearance when frozen

<sup>\*</sup> This suggests an easier method of procuring potassium than has hitherto been practised.

<sup>+</sup> This salt is easily prepared by the process given in this section.

is somewhat similar to that of crystallized nitrate of ammonia. When heated to the temperature of 80° it assumes the gaseous form, and the specific gravity of its vapour, as determined by Gay-Lussac, is 0.9476. Being a compound of 1 volume hydrogen and I volume cyanogen united together without any alteration in volume, it is obvious that the true specific gravity must be the mean of that of cyanogen gas and hydrogen gas.

Sp. gr. of cyanogen gas 0.0694of hydrogen gas 1.8749

> Mean 0.9375

This gives us 0.9375 for the specific gravity of this gas. one of those gases whose specific gravity is obtained by multiplying its atomic weight by 0.2777. Now we shall see immediately that its atomic weight is 3.375 and 3.375 × 0.2777 = 0.9375, the same as before. This calculated specific gravity comes within 1 per cent. of the experimental result.

When the vapour of this acid is mixed with oxygen gas, and an electric spark passed through it, a detonation takes place. For complete combustion, 1 volume of the vapour requires 1.25 of oxygen. The products are 1 carbonic acid mixed with 0.5 azote. I of the oxygen went to the formation of carbonic acid. The remaining 0.25 of oxygen must have combined with hydrogen, and the quantity of hydrogen with which they combined must have been 0.5 Hence it follows that hydrocyanic acid composition. must consist in bulk of 1 volume of carbon vapour, 1 volume of azote, and 1 volume of hydrogen; or, doubling the volumes, of

2 volumes carbon vapour,

1 volume azotic gas,

1 volume hydrogen,

condensed into two volumes. But 2 volumes carbon vapour + 1 volume azotic gas condensed into 1 volume, constitute cyanogen. It is therefore obvious that hydrocyanic acid is a compound of 1 volume of cyanogen and 1 volume of hydrogen gases united together without any alteration of volume whatever.

Anhydrous hydrocyanic acid undergoes spontaneous decomposition even in dry vessels, and though kept in a dark place. Sometimes it is decomposed in a few hours, while at other times it may be kept for a couple of weeks without alteration. The colour becomes first reddish brown; this colour deepens, and a

quantity of the brown charry matter, already repeatedly alluded to, is deposited, with a smell of ammonia. In short, the acid is gradually converted into cyanodide of ammonia and the charry matter.\* This acid when diluted with water may be preserved any length of time provided it be kept from the action of the light. The best way is to put it into a phial covered on the outside with a coating of black paint. If we expose it to the light, even in a close vessel, it undergoes complete decomposition in a very short time.

Action of sulphur.

When sulphur is heated in hydrocyanic acid gas, it absorbs the gas, and if we saturate it with this gas we obtain a yellow coloured solid body having a crystalline texture, which dissolves in water, does not precipitate the salts of lead, and forms with the bases a peculiar genus of salts not hitherto investigated. Phosphorus may be sublimed in hydrocyanic acid gas without undergoing any alteration.

Of heat.

When this acid gas is passed through red-hot iron it undergoes complete decomposition, charcoal being deposited on the iron and a gas evolved, which is a mixture of equal volumes of hydrogen and azotic gas. When potassium is heated in this gas it absorbs the cyanogen and leaves a quantity of hydrogen equal to half the volume of the hydrocyanic acid employed. The cyanodide of potash dissolves in water, and yields when evaporated a white salt exactly similar to that obtained by fusing the common yellow prussiate of potash.

Of alkalies,

The alkalies when placed in contact with hydrocyanic acid occasion a double decomposition. The hydrogen of the acid uniting with the oxygen of the alkali constitutes water, while the metallic bases of the alkali uniting to the cyanogen forms a cyanodide of potassium or sodium. When these cyanodides are exposed to the air (especially when in solution) the potassium or sodium is speedily oxidized at the expense of the air, and the cyanodide is in consequence decomposed. The carbonic acid of the atmosphere gradually unites to the alkali thus formed, and the hydrocyanic acid or cyanogen is disengaged. These cyanodides may be preserved much longer in a solid state. I have kept the cyanodide of potassium for a consider-

<sup>\*</sup> It would appear from the observations of M. Kuhlman, that when hydrocyanic acid is mixed with muriatic acid abundance of crystals of sal ammoniac are almost immediately formed. Ann. de Chim. et de Phys. xl. 441. It is possible that the speedy decomposition of hydrocyanic acid may be partly owing to the presence of some muriatic acid in it, when obtained by Gay-Lussac's process.

able time in a phial without any tendency to decomposition being perceived.

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The deutoxide of manganese absorbs completely the vapour of hydrocyanic acid in a few hours. Water is formed, but cyanogen is not evolved.

When red oxide of mercury is heated in hydrocyanic acid of red oxide of mercury. vapour a violent action takes place, and so much heat is evolved as to destroy the compound formed. When the experiment is made without the application of heat, the vapour is absorbed by the oxide. When the oxide thus saturated with vapour of hydrocyanic acid is heated, water is disengaged, and there remains the substance formerly known by the name of prussiate of mercury. It is obvious from this that a double decomposition takes place, water is formed and cyanodide of mercury.

Hydrocyanic acid is one of the most virulent poisons known. Hydrocyanic acid a violent Some years ago, a chemist, while engaged in preparing it, let a poison. few drops fall upon his arm. It speedily evaporated, yet the unfortunate man fell a victim to the application in the course of two hours.\* When a single drop of it is applied to the eye of a common sized dog or a cat violent convulsions are produced, which speedily terminate in death. It has been long known that ammonia constitutes an antidote to this poison by counteracting its effects. But from the experiments of M. Simeon, + Antidote. confirmed by those of MM. Persoz and Norrat, t it appears that chlorine constitutes a more certain and complete antidote. Being put into the throat of the poisoned animal it speedily relieves the symptoms, and the animal, after an interval of some hours, again recovers its health. Even in one case where the poison had been allowed to exert its action till the animal was at the point of death, the respiration having been stopped for 25 seconds, the application of chlorine restored animation, and the animal recovered.

Hydrocyanic acid when much diluted with water is also a Used in medicine. poison when administered in sufficient quantity. given in small quantities it has been found a valuable medicine in various diseases, and in none does its administration appear to be more beneficial than in dyspepsia. I have found that water holding in solution one per cent. of this acid constitutes a sufficient strength. Of this, as much as a scruple or even half a drachm may be given twice a day. But I have found that about 8 drops of it administered in a glass of water consti-

<sup>\*</sup> Berzelius; Traité de Chimie, ii. 211.

<sup>†</sup> Ann. de Chim. et de Phys. xl. 334.

<sup>‡</sup> Ibid. xliii. 324.

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tutes a sufficient dose. When given in larger doses it diminishes the velocity of the pulse to a very remarkable degree. On one occasion I reduced the pulse of an individual to 23 beats per minute. Upon withdrawing the medicine the pulse gradually resumes its natural velocity. If the use of the medicine be persisted in after the pulse has been thus diminished, the patient is thrown into a state of lethargy similar to that so well described by Shakespeare in the tragedy of Romeo and Juliet. A lethargy of this kind, into which a lady was thrown in Glasgow, continued about 30 hours, and she recovered again without any bad consequences whatever following. I mention these facts to show with what caution so powerful a medicine should be prescribed.

How detected.

Lassaigne has proposed the following method of detecting hydrocyanic acid after death in the stomachs of those who have been poisoned by that baneful drug: The stomach is to be cut in pieces and mixed (together with its contents) with a little water. This mixture is to be distilled by a gentle heat till about one-eighth part of the water has passed over into the To the distilled liquid add a drop of caustic potash, and immediately after a very small quantity of the solution of sulphate of copper. A small quantity of matter will be disengaged by the action of the alkali on the copper solution. Then add one or two drops of muriatic acid. If no hydrocyanic acid be present the whole cupreous precipitate will be dissolved, and the liquid become transparent. But if any hydrocyanate of copper be present it will remain undissolved and of a white colour. By this method  $\frac{1}{20000}$ th part of the liquid of hydrocyanic acid may be detected. There is, however, a source of ambiguity. The same white precipitate will remain if the liquid should contain hydriodic acid. Sulphate of iron when substituted for sulphate of copper will detect Tologoth of the weight of the liquid of hydrocyanic acid, but it has the advantage of being characteristic in consequence of the formation of prussian blue.\* If the quantity of hydrocyanic acid present be very small the hydrocyanate of copper is redissolved in the course of a few hours.

The same difficulty occurs in determining whether hydrocyanic acid unites with bases, as was mentioned before respecting muriatic acid. Yet I think that the phenomena leave little doubt that no such class of salts as hydrocyanates exist.

But that whenever this acid comes in contact with an oxide a double decomposition takes place, water being formed while the cyanogen and the metallic base uniting constitute a cyanodide.

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# SECTION III. - OF CYANOUS ACID.

I have been induced to give this name to the acid first dis-History. covered and described by M. Wöhler, under the name of cyanic acid,\* in consequence of the subsequent discovery by Serullas of another compound of cyanogen and oxygen, which contains twice as much oxygen as Wöhler's acid.† To this last acid we must, according to the rules of nomenclature, apply the name cyanic acid.

The existence of cyanous acid was first suspected by Vauquelin. He observed that when water impregnated with cyanogen was set aside it underwent spontaneous decomposition, being converted into carbonic acid, hydrocyanic acid, charry matter, ammonia, and a particular acid which he proposed to distinguish by the name of cyanic acid.

Wöhler found that when a current of cyanogen gas was passed into barytes water containing undissolved crystals of hydrate of barytes, the liquid assumed a brown colour, and charry matter was deposited while the barytes dissolved. After the process was over, he passed a current of carbonic acid gas through the liquid to decompose any hydrocyanate of barytes that it might contain. It was then boiled to drive off the hydrocyanic acid and concentrated after filtration. A white salt was obtained in silky needles, which was cyanite of barytes. In his paper on this subject, he examined the properties of this cyanite and of several others which he obtained; but he did not succeed in procuring the cyanous acid or in analyzing it. But finding that water and his acid by mutual decomposition were converted into carbonic acid and ammonia, he concluded that his acid was a compound of

I atom cyanogen, I atom oxygen.

1 cyanous acid contains 3 water contains .	•	Oxy. Carb. Azote. Hyd $1 + 2 + 1$ $3 + 0 + 0 + 3$	
Total atoms .		4+9+1+9	

<sup>\*</sup> Gilbert's Annalen, lxxi. 95.

<sup>†</sup> Ann. de Chim. et de Phys. xxxviii. 379. ‡ Ibid. ix. 113; xxii. 132.

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2 carbonic acid contains 1 ammonia contains .	•	4 +	2	Azote,	•
		4 +	2 +		- 3

It is evident from this that one atom of cyanous acid and three atoms of water may be converted into an integrant particle of bicarbonate of ammonia.

Formation.

Wöhler found afterwards that the easiest method of procuring cyanite of potash was to reduce anhydrous ferroprussiate of potash to a fine powder, and mix it intimately with about its own weight of black oxide of manganese. This mixture is to be heated in a silver crucible to incipient ignition.\* matter which has been thus heated is to be boiled in alcohol of the specific gravity 0.832. The alcoholic solution as it cools deposites cyanite of potash in small scales, similar in appearance to chlorate of potash.+ He now subjected the acid to analysis, and confirmed his former opinion of its constitution. Wöhler's attempts to obtain this acid in a separate state were unsuccessful; but Liebig pointed out a process by which it might be procured nearly pure, and so that its characters could be recognised. † His analysis at first differed from that of Wöhler, but he afterwards satisfied himself that Wöhler's determination was correct.

Cyanous acid may be obtained by the following process: Mix together solutions of cyanite of potash and nitrate of silver. The cyanite of silver precipitates in the state of a white powder. which is nearly insoluble in water. Suspend this evanite in water, and pass through the liquid a current of sulphuretted hydrogen gas, taking care not to add enough to decompose the whole cyanite of silver employed. The silver is thrown down in the state of sulphuret, and the cyanous acid dissolves in the Let the sulphuret of silver and undecomposed cyanite subside, and then decant off the clear liquid, which constitutes an aqueous solution of cyanous acid. This liquid has a sour taste, and reddens vegetable blacs. Its smell is compared by Wöhler to that of acetic acid. When left in contact with water it undergoes spontaneous decomposition in a few hours, being converted into carbonate of ammonia.§ It combines

Properties.

<sup>\*</sup> Too great a heat destroys the acid.

<sup>†</sup> Ann. de Chim. et de Phys. xxvii. 196; and Gilbert's Annalen, lxxiii. 157.

<sup>‡</sup> Ann. de. Chim. et de Phys. xxxiii. 207.

<sup>§</sup> Liebig, Ann. de Chim. et de Phys. xxxiii. 208.

with the different bases, and neutralizes them, constituting cyanites, some of which have been examined, and will be described in a subsequent part of this work.

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To determine the atomic weight of this acid, Wöhler analyzed cyanite of potash and cyanite of silver.\* He found them composed as follows:

1. C	yanite o	f pota	ısh.		Atomic
Cyanous acid	•	•	•	4.353	weight.
Potash .	•	•	•	. <b>6</b>	
2. (	Zyanite (	of silv	er.		
Cyanous acid	•	•	•	<b>4·34</b> 8	
Oxide of silver	•	•	•	14.75	

The mean of the two numbers attached to cyanous acid is 4.35, which therefore is the atomic weight of this acid as derived from the experiments of Wöhler. To determine the composition of this acid he decomposed a given weight of cyanite of silver by means of muriatic acid, which converts the carbon in the acid into carbonic acid gas. The volume of carbonic acid gas being measured gave him the weight of carbon, which the acid in the salt contained. Cyanogen being a compound of 1.5 by weight of carbon and 1.75 of azote, it was easy to infer the weight of azote in the acid. What was wanted to make up the whole weight of the acid was considered as oxygen. In this way he determined the constituents of cyanous acid to be

this way	ne determined	i me c	OHSOLO	uenu	OI	cyanous acid	w be	
•	Carbon	•	•	•	;	35.334		Composition.
	Azote	•	•	•		41.317		
	Oxygen	•	•	•	•	23.349		
						<del></del>		
					1	00.000		
This is o	bviously equiv	valent	to					
	2 atoms ca	rbon				1.5		
	l atom azo	ote		,	•	1.75		
	1 atom oxy	ygen	•	•	•	1.		
				•				
						4.25		

So that, according to this analysis, the true atomic weight of cyanous acid is 4.25, and it is a compound of 1 atom cyanogen and 1 atom oxygen.

#### SECTION IV .- OF CYANIC ACID.

This acid was discovered by Serullas in 1829. He obtained History. it by dissolving a substance, which he called *perchloride of* 

<sup>\*</sup> Ann. de Chim. et de Phys. xxvii. 196.

cyanogen, and which will be described in a subsequent section, in hot water, and boiling the solution for some time. By the action of the hot water the perchloride is converted into muriatic acid and cyanic acid. By evaporating the liquid the muriatic acid is driven off, and the cyanic acid is deposited in crystals.\*

Properties.

Cyanic acid thus obtained is a white solid which crystallizes in brilliant transparent rhombs. When heated it sublimes, and is then deposited in fine needles. It has but little taste, yet it reddens vegetable blues. It is but little soluble in cold water; but hot water is a better solvent of it. Its specific gravity is rather less than 1.847. For it floats in concentrated sulphuric acid, but falls down when that acid is slightly diluted with water. It requires for volatilization a heat rather greater than is sufficient to boil mercury. When strongly heated a portion of it is decomposed, charcoal being left. If it contains moisture carbonate of ammonia is evolved in proportion to the quantity of moisture present.

Nitric acid has no action on it whatever, excepting that it dissolves it when assisted by heat. It is equally soluble in sulphuric acid, but without undergoing decomposition or alteration. When placed in contact with potassium combination takes place, cyanodide of potassium and potash being formed.

This acid combines with bases, and produces a genus of salts which have been distinguished by the name of cyanates. But these salts have not yet been subjected to examination.

From the trials of M. Serullas, this acid seems to have no very striking or injurious effect on the animal economy. Two grains mixed with water were introduced into the esophagus of a rabbit, but occasioned no sensible inconvenience.

M. Serullas analyzed this acid by heating it with oxide of copper. The gas extricated was a mixture of two volumes carbonic acid and I volume of azote. The loss of weight wanting to make up the sum total of the acid was considered as oxygen. From this analysis the constituents were deduced as follows:

Composition.

Carbon	•		•	28.56
Azote		•	•	33.30
Oxygen	•	•	•	38.14

100.00

This is obviously equivalent to

<sup>\*</sup> Ann. de Chim. et de Phys. xxxviii. 382.

2 atoms carbon	•	•	1.5	Class VI.
l atom azote		•	1.75	Sect. V.
2 atoms oxygen	•	•	<b>2</b>	

5.25

It is therefore a compound of an atom of cyanogen and 2 atoms of oxygen, and its atomic weight is 5.25. It contains just twice the quantity of oxygen that cyanous acid does, and is obviously a much more intimate and permanent compound.

#### .SECTION V .--- OF FULMINIC ACID.

In the year 1800, Mr. Howard published in the Philosophical History. Transactions,\* a process for making fulminating mercury, together with an account of some of the most remarkable properties of this substance. His process was as follows: In a measured ounce and a half of nitric acid of the specific gravity 1.3, dissolve by means of heat 100 grains of mercury. Pour this solution upon two measured ounces of alcohol, and apply heat till the mixture begins to effervesce. The heat is then to be The action becomes violent, and continues for some time; a dense white smoke issues from the vessel, which is heavier than the atmospheric air, and may be poured into glassjars, where it continues for some time like fine white clouds. Meanwhile a white powder falls to the bottom of the mixture. When the effervescence is over, this white powder is to be separated by filtration, washed with pure water, and dried in a heat not exceeding 212°. This white crystalline powder constitutes fulminating mercury. This powder explodes when heated to It explodes also loudly when it is wrapt up in paper and struck upon an anvil.

Soon afterwards, Mr. Howard, assisted by Mr. Cruikshanks of Woolwich, formed fulminating silver by a similar process. The best method of forming this formidable compound is the following: Dissolve a drachm of pure silver in an ounce and a half of nitric acid of the specific gravity 1.52 (or acid of only 1.42 or 1.35 will do), to this solution add two ounces of alcohol of the specific gravity 0.85, and bring the mixture (put into a flask) gradually to a boiling heat. As soon as an effervescence begins, white crystalline flocks make their appearance. The vessel must now be put in a cool place and left at rest, till the effervescence, which continues for some time, is at an end.

During this time the quantity of precipitate greatly increases; and if we wish to have as great a quantity of fulminating silver as possible, we ought to cool it artificially. Fulminating silver thus prepared, is a much more formidable substance than fulminating mercury. It dissolves in 36 times its weight of hot water, and crystallizes on cooling. It has a metallic taste, and blackens the skin like other salts of silver. When exposed to the light it becomes first reddish, and at last nearly black. This formidable compound, as usually prepared, is in the state of a powder. It detonates much more loudly than fulminating mercury.\*

These two formidable substances had been known to chemists, and had been repeatedly exhibited for more than 20 years, without any attempt to ascertain their nature. At length in the year 1823 they attracted the attention of M. Liebig. He showed that they consisted respectively of the oxide of mercury and of silver, united to a peculiar acid, which he showed to possess a striking analogy with hydrocyanic acid. To this acid he gave the name of fulminic, and he showed that it was capable of combining with the different bases, and of forming salts, which possess the remarkable property of fulminating. He even made a set of experiments to determine the component parts of this acid; but as he afterwards discovered that these original experiments were erroneous, it is unnecessary to specify them here.

He repeated his experiments with more exactness in the laboratory of M. Gaultier de Claubry, in Paris, and carried his investigations a good deal farther; but still without reaching the requisite degree of accuracy.‡ In the year 1824, a very elaborate and ingenious set of experiments, to determine the constituents of fulminic acid, was made by MM. Gay-Lussac and Liebig together.§ The conclusion to which they came was, that the composition of fulminic acid is identical with that of cyanous acid; namely:

1 atom cyanogen . . 3.25 1 atom oxygen . . 1

4.25

But to this conclusion it may be objected that the properties of fulminic acid and of cyanous acid are quite different. All the compounds of the first acid and bases fulminate by heat or

<sup>\*</sup> Phil. Trans. 1800, p. 285. † Gilbert's Annalen, lxxiii. 393.

<sup>‡</sup> Ann. de Chim. et de Phys. xxiv. 294. § Ibid. xxv. 285.

friction, while the compounds of cyanous acid and bases have no fulminating properties whatever.

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In the year 1826, a new paper on the subject was published by M. Liebig, in which he endeavoured to explain what takes place when a fulminate is decomposed by sulphuretted hydrogen gas.\*

It was about this time that the attention of Mr. Edmund Davy was drawn to these curious salts, and as the Dublin Society, to which he is professor of chemistry, are not supplied with the continental journals, he presecuted his investigations for a considerable time before he became aware of the previous investigations of Gay-Lussac and Liebig. Meanwhile he discovered that fulminating mercury and silver contain a peculiar acid, which he found the method of combining with the different bases. He examined the properties of these different salts, analyzed the fulminates of silver and mercury, by which the atomic weight of the acid was determined, and after several unsuccessful trials, at last hit upon a method of obtaining the fulminic acid free from a base, and only dissolved in water. Finally, he analyzed fulminic acid, and obtained results somewhat different from those of Gay-Lussac and Liebig.+

Such is the history of the investigation of this very curious substance. It is now time to describe the method of obtaining it, and the properties by which it is characterized.

Fulminic acid was obtained in a separate state by Mr. Davy, Preparation. by the following process: Put into a bottle with a ground stopper, a quantity of fulminating mercury, together with about twice its weight of clean zinc filings, and about three quarters of a fluid ounce of water for every 20 grains of fulminating mercury employed. If the bottle be kept in a temperature of about 80°, and occasionally agitated, the fulminating mercury is soon decomposed, and a solution of fulminate of zinc obtained. This liquid is to be filtered into another bottle, and about onethird of its bulk of a saturated aqueous solution of barytes is to be added. When the mixture is agitated, the oxide of zinc is precipitated, and a solution of fulminate of barytes formed. Filter the fulminate of barytes into another stoppered bottle, and add just the quantity of sulphuric acid (previously diluted

<sup>•</sup> Ann. de Chim. et de Phys. xxv. 285.

<sup>†</sup> Mr. Davy's paper was printed in Transactions of the Royal Dublin Society for 1829. I do not know whether the volume be yet published. But Mr. Davy was so very obliging as to send me a copy of his paper during the summer of 1830.

<sup>‡</sup> If too much barytes be added the oxide of zinc is again redissolved.

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with water) that is requisite to saturate the barytes. Shake the mixture, and then filter to separate the sulphate of barytes, and let the solution of fulminic acid thus procured, be collected into another bottle with a ground stopper.

Properties.

Fulminic acid thus obtained is a colourless and transparent liquid. Its taste is at first sweet, which is followed by a particular astringency, and it leaves an unpleasant impression on the palate, and excites expectoration. Its smell is pungent and disagreeable, having some resemblance to that of concentrated hydrocyanic acid. It reddens vegetable blues, and if a blue paper be suspended over the fluid in a bottle, it gradually acquires a deep red colour, and a sweetish astringent taste. Mr. E. Davy considers it as very poisonous; even exposure to the fumes of it excited headach. It is volatile; when exposed to the air it rises in vapour, emitting its peculiar smell, and if the vessel in which it is placed be covered with a piece of glass, moistened with nitrate of silver, small crystals of fulminate of silver soon make their appearance on it.

Fulminic acid combines with the different bases, and forms a class of salts called fulminates. From these salts it is expelled by sulphuric, nitric, phosphoric, oxalic acids, &c., muriatic acid, even when dilute, decomposes it. It gives no precipitate when mixed with solutions of barytes or the alkalies. But nitrates of silver and mercury form with it fulminates of these bases. Nitrate of silver is a very delicate test of it, forming a precipitate of fulminate of silver, even when the acid is present in only a minute quantity.

When first prepared fulminic acid is colourless; but it acquires a yellow colour in the course of a few hours. This change takes place whether the acid be kept in the dark or exposed to the light. But it appears most speedily when heat is applied. When it becomes yellow its sweet taste disappears, and it becomes more astringent; a very minute quantity of yellow powder falls, and then it loses its pungent odour.

Atomic weight. To determine the atomic weight of this acid, fulminating silver was analyzed by Mr. E. Davy. He found it composed of

Fulminic acid . . . 5.25 Oxide of silver . . . . 14.75

20

According to this analysis the atomic weight is 5.25. He found the constituents of fulminate of mercury

Fulminic acid	•	•	28.76 or 5.21	Class VI.
Oxide of mercury	•	•	71.24 or 13	Sect. V.

## 100.00

This would make the atomic weight 5.21, which is within less than one per cent. of the former number.

But with this determination the experiments of Gay-Lussac and Liebig do not accord. They find the atomic weight 4.25, instead of 5.25. The composition of the acid, as determined by these two chemists, is as follows:

l atom cyanogen	•	•	3.25
1 atom oxygen	•	•	1

#### 4.25\*

Mr. Davy, on the contrary, finds the composition as follows: composition.

<b>2</b>	atoms	carbon	•	•	1.5
110	atom	azote .	•	•	2.625
1	atom	hydrogen	•	•	0.125
-		oxygen	•	•	1.000

5.25

This analysis differs from that of Gay-Lussac and Liebig by

-	$\frac{1}{\alpha}$ atom azote	•	•	0.875
1	atom hydrogen			0.125

1.

The experiments of Gay-Lussac and Liebig seem to be decisive respecting the proportion between the volumes of azotic gas and carbonic acid gas, which are obtained when this acid is decomposed by means of oxide of copper; provided their apparatus, which was rather complicated, did not mislead them. However, the want of similarity in the results which they obtained, together with the certainty that fulminic acid differs completely from the cyanous acid of Wöhler (with which their analysis would render it identical), incline me to prefer the analytical results of Mr. Davy, according to which the fulminic acid differs from the cyanous, by containing \(\frac{1}{2}\) atom of azote. The atom of hydrogen which Mr. Davy considers as another constituent is not so well established. Gay-Lussac and Liebig have been at great pains to prove the absence of hydrogen, and I think their reasoning at least very plausible. I more than

<sup>\*</sup> Ann. de Chim. et de Phys. xxv. 285.

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suspect that in Davy's experiments a little hygrometrical moisture may have insinuated itself into the fulminate before it was heated. I think Davy's processes were simpler, and therefore more susceptible of accuracy than those of Gay-Lussac and Liebig. But the want of coincidence will render it very desirable that the analysis of this formidable acid should be repeated by some other person, with a view of determining on which side the truth lies.

SECTION VI.—OF CHLOROCYANIC ACID, OR CHLORIDE OF CYANOGEN.

History.

The existence of this compound was first recognised by Berthollet, who gave it the name of oxyprussic acid. Its real nature was first ascertained by Gay-Lussac, in the year 1815.\* He gave it the name of chlorocyanic acid.

He prepared this acid by passing a current of chlorine gas through a solution of hydrocyanic acid in water till the liquid discoloured indigo dissolved in sulphuric acid. He then deprived it of the excess of chlorine which it contained, by agitating it with mercury. To separate chlorocyanic acid from this liquid, he took a glass cylinder, filled in two-thirds full of mercury; it was then filled to the brim with the hydrocyanic acid, saturated with chlorine, and inverted into a basin of mercury. This basin, with the cylinder in it, was put under the receiver of an air-pump, and the air of the receiver drawn out till the whole of the mercury, and even of the liquid, was displaced, and the cylinder filled with chlorocyanic acid in the state of an elastic vapour. On letting the air into the receiver, the vapour was condensed into a liquid, and the mercury again made its way into the cylinder. By this process, however, the compound was only obtained in a state of impurity. Serullas first pointed out the method of obtaining it pure, and gave an accurate account of its properties in the year 1827.+

Preparation.

It may be prepared by the following process: Fill a bottle or flask, capable of holding about 60 cubic inches, with chlorine gas, and then put into it from 77 to 90 grains of cyanodide of mercury. As much water is now to be introduced as will reduce the cyanodide to a magma; but not dissolve it. The vessel must now be placed in the dark. In about 6 or 10 hours a double decomposition will have taken place; the mercury will be converted into corrosive sublimate, and the cyan-

<sup>\*</sup> Ann. de Chim. xcv. 136. † Ann. de Chim. et de Phys. xxxv. 291.

ogen combined with chlorine will fill the vessel in the state of Class VI. If the flask be now surrounded with a freezing mixture, composed of 2 parts of snow and 1 part of salt, the chloride of cyanogen is converted into solid crystals, which attach themselves to the sides of the flask. While the flask is in the freezing mixture, introduce into it a quantity of dry chloride of calcium to absorb all the water, and corking the vessel, leave it in this state for two or three days. Then surround it again with a freezing mixture, and when the chloride has crystallized, withdraw the chloride of calcium, and fill the flask with mercury, previously cooled down to zero. a bent tube into the mouth of the flask; plunge the tube into a mercurial trough, and cautiously heating the flask by means of a few pieces of burning charcoal, placed near it, the chloride fuses and effervesces, and passes over rapidly into the mercurial trough, where it is to be received in jars previously filled with mercury, and ready prepared for the purpose.

Chloride of cyanogen at zero is a transparent solid, which Properties. crystallizes in long transparent needles. It liquefies when heated up to the temperature of about 15° or 16°. The gas liquefies at the temperature of 68° when exposed to a pressure of four atmospheres. At the ordinary temperature of the air it is gaseous. No attempts have been made to determine its specific gravity in the gaseous state. But it is obvious that it must be the mean of the specific gravity of cyanogen and chlorine gases, or 2.1527. Its smell is extremely offensive and deleterious.

At the temperature of 68° water absorbs 25 times its volume of this gas, sulphuric ether absorbs 50 times its volume, and alcohol 100 times its volume. These solutions may be preserved any length of time without alteration. When pure it does not precipitate nitrate of mercury, nor produce any alteration on vegetable blues. Nor does it seem capable of combining with bases; at least we have no evidence that it can be united with them. Potash when added to its aqueous solution occasions its decomposition, carbonic acid and ammonia being formed. We have therefore no evidence that it possesses acid properties. On that account the term chloride of cyanogen is a more appropriate name for it than chlorocyanic acid.

It has the property of throwing down iron from its solutions, of a green colour. The method of proceeding is to pour chlordcyanic acid into a solution of iron, to this mixture a little potash is added, and, finally, a little acid, which produces the precipiChap, I.

tation of the iron. This property was recognised by Berthollet, and induced him to consider chloride of cyanogen as a peculiar body.

This substance is very caustic; even when it comes for an instant in contact with any part of the body deprived of the skin, while in the state of gas, a feeling of great pain takes place. It is also exceedingly deleterious. About a grain of it dissolved in water being introduced into the throat of a rabbit, occasioned instant death.

Composition.

It was analyzed in a very ingenious manner by M. Gay-Lassac, who showed it to be a compound of

1 volume cyanogen gas . . . 3.25 1 volume chlorine gas . . . 4.5

7.75

united together without any alteration of volume.\* This analysis was repeated and confirmed by Serullas, who employed pure chloride of cyanogen. It is obvious, therefore, that its atomic weight is 7.75, and that its specific gravity is the mean of that of its two gaseous constituents, or it is the atomic weight multiplied by 0.2777. For  $0.2777 \times 7.75 = 2.1527$ , which is exactly the mean of that of the two constituents.+

SECTION VII. -- OF PERCHLORIDE OF CYANOGEN.

History.

This compound was also discovered by M. Serullas, by prosecuting the experiments detailed in the last section. It may be obtained by the following process:

Preparation.

Fill a bottle capable of holding about 65 cubic inches with dry chlorine gas, and after putting into it about 15 grains of pure liquid hydrocyanic acid, shut up the mouth of the bottle with a ground stopper, expose it to the direct rays of the sun. The colour of the chlorine gradually disappears, and a colourless liquid like water begins to appear on the sides of the bottle. This liquid gradually thickens, and at last solidifies into a white matter interspersed with small brilliant crystals. The bottle must be allowed to remain three or four days before it be opened, in order to be sure that the decomposition has been carried far enough. Then the bottle being opened, the muriatic acid gas is to be blown out by means of a pair of bellows. Then introduce a little water and a good many fragments of glass, in order by agitation to detach the solid matter from the

<sup>\*</sup> Ann. de Chim. xcv. 200. † Ann. de Chim. et de Phys. xxxv. 342.

sides of the vessel. Agitate well, then throw the whole contents into a dish; pick out the pieces of glass, and break the white matter with a glass rod to allow it to be washed. Wash it two or three times with small quantities of cold water. Press the white matter thus washed between folds of blotting paper to make it as dry as possible. Introduce it now into a small retort, and heat it till it fuses. Then distil it over into the receiver. It passes over in the state of a transparent colourless liquid, which crystallizes in the beak of the retort and in the receiver. To render it quite pure it ought to be distilled a second time.

Perchloride of cyanogen thus obtained is a very white sub-Properties. stance, which crystallizes in needles. Its odour is strong and disagreeable, and excites tears, especially if the perchloride be heated. Serullas compares the smell to that of mice. Its taste is sharp, but not strong. Its specific gravity is about 1.320. It melts when heated to 284°, and boils at the temperature of 374°.

It is very little soluble in cold water. Hot water dissolves it much better, and the solution speedily undergoes decomposition, being converted into muriatic and cyanic acid. The same decomposition takes place slowly, if the perchloride be left in contact with cold water. Two atoms of water are decomposed, the hydrogen of which converts the chlorine into muriatic acid, while the oxygen converts the cyanogen into cyanic acid.

Perchloride of cyanogen dissolves readily in alcohol and ether. It is a very virulent poison—a grain of it dissolved in alcohol being introduced into the esophagus of a rabbit, caused instant death. Another grain was put into 30 grammes of water, which was filtered to separate the undissolved portion, and then given to another rabbit. The animal died in 25 minutes.

M. Serullas, in order to determine its composition, mixed a composition. portion of it with caustic potash, then heated it with an excess of nitric acid, and threw down the chlorine by means of nitrate 12.25 grains of it were found to yield nine grains of chlorine. To determine the other constituents it was heated with oxide of copper, and the proportion of carbonic acid and azotic gases evolved measured. Though this last part of the analysis did not come out correct, yet from the way in which this perchloride is decomposed when it is left in contact with water, and from the quantity of chlorine which it contains, there

Chap. I. can be no doubt that it is a compound of

1 atom cyanogen . . 3.25 2 atoms chlorine . . 9

Hence its atomic weight is 12.25, and it contains just twice as much chlorine as the chloride described in the last section. Whether it be capable of combining with bases cannot be easily determined, in consequence of the decomposition which it undergoes when dissolved in water. • But it is probable that its properties in this respect do not differ much from those of the chloride.\*

#### SECTION VIII. -- OF BROMIDE OF CYANOGEN.

History.

This compound, like the two preceding, was discovered by M. Serullas. The process which he employed is the following: Put into the bottom of a long glass tube, shut at one end, two parts of cyanodide of mercury, plunge the bottom of the tube into a freezing mixture, or at least into cold water, and then pour on the cyanodide one part of bromine. The action is violent, and much heat is evolved. There are formed bromide of mercury and bromide of cyanogen, which last substance crystallizes in long needles in the upper part of the tube amidst a little vapour of bromine, which is gradually dissipated by coming in contact with the cyanodide of mercury. Adapt a small receiver to the tube, and surround it with a freezing mixture. Then by means of a gentle heat the bromide of cyanogen is driven into the receiver where it crystallizes.

Properties.

The crystals are sometimes very small transparent cubes, sometimes very slender and long needles. Its smell is very strong and disagreeable. It is very volatile, and when heated up to the temperature of about 60°, it assumes the form of a gas. When again cooled down it crystallizes as before.

It dissolves both in water and alcohol more readily than iodide of cyanogen. When mixed with a solution of caustic potash it undergoes decomposition, being converted into hydrocyanate and hydrobromate of potash.

Bromide of cyanogen is exceedingly poisonous. A grain dissolved in a little water, and introduced into the œsophagus

<sup>\*</sup> Serullas, Ann. de Chim. et de Phys. xxxviii. 370.

<sup>†</sup> This is the statement of Serullas; but it is obvious that the oxygen of the water must have combined either with the cyanogen or bromine, so that the liquid must contain either cyanic or bromic acid.

of a rabbit produced instant death. This bromide has not been analyzed. But from the complete analogy existing between it and the chloride and iodide of cyanogen, there can be no doubt that its constituents are

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1 atom cyanogen . 3.25 1 atom bromine . 10

13.25

and that its atomic weight is 13.25.\*

When three parts of bromine and one part of hydrocyanic Perbromide. acid are left in contact, we obtain a solid compound of bromine and cyanogen different from the preceding, and distinguished by that peculiar smell of mice which characterizes the perchloride of cyanogen. Serullas, to whom we are indebted for our knowledge of this compound, conjectures that it is a perbromide of cyanogen or a compound of

1 atom cyanogen . . 3.25 2 atoms bromine . . 20

23.25+

#### SECTION IX. -- OF IODIDE OF CYANOGEN.

For this compound likewise we are indebted to the sagacity History. and industry of Serullas. He obtained it by the following process:

Two parts of dry cyanodide of mercury and one part of dry Preparation. iodine were triturated together in a glass mortar, and then introduced into a wide-mouthed phial, which was exposed to heat gradually increased till the cyanodide of mercury began to undergo decomposition. Decrepitation, the disappearing of some violet vapours of iodine, and the commencement of the condensation of a white matter at the mouth of the phial were the indications of this decomposition. Then the phial was taken up in a pair of pincers and introduced under a large glass jar placed inverted on a glass plate, and lifted up at one edge to admit the phial which was inclined somewhat as if to pour something out of its mouth. White vapours issued rapidly and condensed on the glass disc like flocks of cotton. When these flocks ceased to issue the phial was again heated, and the flocks poured out as before; and this was repeated as long as these white flocks continued to be formed. These white flocks constituted the jodide

<sup>\*</sup> Serullas, Ann. de Chim. et de Phys. xxxiv. 100. † Ibid. xxxviii. 374.

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of cyanogen. To obtain it quite pure it is necessary to sublime them. This was done by putting them into the bottom of a long glass tube, shut at one end, which was plunged in boiling water, and kept in it, while the upper part of the tube was bent a little. The iodide gradually sublimed into the upper part of the tube, while some iodide of mercury remained at the bottom.

Properties.

Iodide of cyanogen thus obtained is white, and is crystallized in very slender but long needles. Its smell is powerful, irritating the eyes and causing a flow of tears. Its taste is excessively caustic. Its specific gravity is greater than that of sulphuric acid, through which it falls rapidly. It is volatile, and may be exposed to a higher temperature than that of boiling water without undergoing decomposition. When thrown on burning coals violet vapours are given out in abundance. It is soluble in water and in alcohol. These solutions produce no alteration on vegetable blues. When caustic potash is added to the aqueous solution the iodide is immediately decomposed, hydriodate and hydrocyanate of potash being formed.

Nitric acid has no action on it. Sulphuric acid is not imme-

Nitric acid has no action on it. Sulphuric acid is not immediately affected by it. But after a certain time it acquires a red colour, and iodine is precipitated. Muriatic acid decomposes it, iodine being precipitated, and hydrocyanic acid formed. Sulphurous acid decomposes it immediately. Iodine is disengaged, and hydriodic acid, hydrocyanic acid, and sulphuric acid, are formed. It is obvious also from the phenomena described by Serullas, that some substance analogous to chloride of cyanogen is formed, as sulphate of iron is precipitated green, after all the sulphurous acid and hydrocyanic acid has been driven off by heat. If sulphurous acid gas be quite dry it has no action on this iodide; the presence of moisture is necessary before the action takes place. Neither has dry chlorine gas any action on it, at least at the ordinary temperature of the atmosphere.

Serullas made a set of experiments to determine its composition by ascertaining the quantity of iodine which it contains. He found that one part of the iodide contains 0.8066 part of iodine. According to this result its composition is

Cyanogen . . . 3.25 Iodine . . . 13.55

Though the quantity of iodine obtained is rather less than an atom, yet considering the striking analogy which this substance bears to the chloride of cyanogen, there can be no reasonable doubt that the true composition is

I atom cyanogen . . 3.25
I atom iodine . . 15.75

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19

and that its atomic weight is 19.\*

This iodide seems much less deleterious than either the bromide or chloride of cyanogen. Serullas tasted it repeatedly, and both he and several other individuals were exposed to the fumes of it without experiencing any other inconvenience than a prostration of strength, and the disagreeable irritation with which it affected the eyes.

### SECTION X .-- OF HYDROSULPHOCYANIC ACID.

This acid was discovered by Mr. Porrett in 1808, and an History. account of it published by him soon after, under the name of prussous acid, because he considered it as differing from common prussic acid by containing less oxygen.+ He afterwards ascertained that it contained sulphur, and published a detailed account of its properties, in the year 1814, under the name of sulphuretted chyazic acid, considering it as a compound of hydrocyanic acid and sulphur.‡

But though it is to Mr. Porrett's ingenious experiments that the chemists of Great Britain and France were indebted for their first knowledge of this acid, it appears from a paper of Berzelius\( \) that it was known long before in Germany, though it had drawn but little of the attention of chemists. In a paper published by Winterl in 1790 on the mode of preparing prussiate of potash, he affirmed that if the mixture of blood and potash from which this prussiate is made be charred without exposure to a red heat, a new compound is formed which may be extracted by alcohol. This, he says, is a compound of potash and a new acid which he calls acid of blood (blutsaure), and which he said might be thrown down in the form of a white powder by means of muriatic acid.

Bucholz found in 1799 that if prussiate of potash be distilled with sulphuric acid, we obtain towards the end of the process an acid which has the smell of the hydrocyanic, but

<sup>\*</sup> Ann. de Chim. et de Phys. xxvii. 184.

<sup>†</sup> Published in the 27th volume of the Transactions of the Society for the Encouragement of Arts, Manufactures, and Commerce. From which it is copied into the Phil. Mag. xxxvi. 196.

<sup>‡</sup> Phil. Trans. 1814, p. 527.

<sup>§</sup> Kong. Vetens. Acad. Handl. 1820, p. 82.

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which colours ferruginous salts red without occasioning any precipitate in them. He considered this new acid as a modification of hydrocyanic acid, and thought that it might be obtained by the action of alcohol on ordinary prussiate of potash.

In 1804 Rink repeated the experiments of Winterl. He found that besides common prussiate of potash another salt is obtained soluble in alcohol. The properties of which he describes, and from his description it is obvious that the acid of this salt was precisely the same as the sulphochyazic acid of Porrett.\*

Mr. Porrett's process for obtaining this acid was very complicated and tedious, but in 1817 Grotthuss proposed another which is much easier.† It consisted in mixing ferroprussiate of potash and sulphur, and fusing the mixture in an open crucible; and he recommends exposing the mixture to a very high temperature.

Soon after Vogel repeated the experiments of Grotthuss, and found that his process succeeded very well, but that the mixture ought not to be exposed to so high a temperature as Grotthuss had proposed. He recommends to fuse the mixture of ferroprussiate of potash and sulphur in a phial, and to keep it in fusion during half an hour.

Berzelius made a set of experiments to determine the temperature necessary for causing a combination to take place between the cyanogen and the sulphur. He found that it commenced as soon as the sulphur began to melt, and that it was speedily completed. If the mass was kept in fusion that portion of the sulphocyanogen, which was in combination with the iron, underwent decomposition, and sulphuret of iron was formed.

Preparation.

The process by which this acid may be most conveniently made is the following: Mix together intimately by trituration equal weights of flowers of sulphur and ferroprussiate of potash, previously deprived of its water and reduced to a fine powder, and fuse the mixture over a spirit-lamp at a temperature approaching to a red heat. When the fused mass has become cold dissolve it in water, and drop into the solution caustic potash till the oxide of iron has been all thrown down. It is then filtered. Evaporate the colourless liquid thus obtained to dryness, and dissolve the dry residue in as little water as pos-

<sup>\*</sup> Gehlen's Jour. ii. 460. + Schweigger's Jour. xx. 225. ‡ Ibid. xxiii. 15.

sible. Mix this solution in a glass retort with a quantity of class VI. concentrated phosphoric acid, and distil. Hydrosulphocyanic Sect. X. acid passes into the receiver.

The acid thus obtained has an exceedingly sour taste. It is Properties. transparent and colourless, and has an odour as strong, and a little resembling that of acetic acid. Its specific gravity, in the most concentrated form in which it was obtained by Mr. Porrett, was 1.022. At a boiling heat it dissolves a little sulphur. The greatest portion of this substance precipitates again when the liquid cools. The presence of sulphur in solution in it may be detected by nitrate of silver, which the acid, while pure, throws down white; but the colour of the precipitate is dark when the acid contains sulphur dissolved in it. It crystallizes when cooled down to the temperature of 14°. It boils at the temperature of 216½°, and at that temperature it is converted into vapour but not into gas. When the acid is thrown into a red hot platinum crucible, sulphur is disengaged, and at last burns with a blue flame. M. Vogel passed the acid through a red hot porcelain tube, and obtained at the farther end of it sulphur, hydrosulphocyanic acid undecomposed, and hydrocyanic acid, which was partly saturated with ammonia. If the tube be filled with iron turnings, sulphuret of iron is formed, and hydrocyanic acid and sulphuretted hydrogen disengaged.

Berzelius proposes the following as the easiest method of obtaining this acid diluted with water: Mix the sulphocyanate of potassium with nitrate of silver or nitrate of mercury. Wash the precipitate and mix it while still moist with water, through which a current of sulphuretted hydrogen gas is to be passed. The silver or mercury is converted into sulphuret, while the hydrosulphocyanic acid dissolves in water. We may get rid of the sulphuretted hydrogen remaining in the liquid either by a gentle evaporation, or by adding small quantities of the original precipitate kept for the purpose till the hepatic smell disappears. Should this acid ever be introduced into medicine, it might be prepared by a process similar to that of Mr. Clark, for preparing hydrocyanic acid, which I have given in a preceding section. It possesses poisonous qualities, but is much less energetic than hydrocyanic acid.

It combines with bases, and forms a set of salts, to which the name of sulphocyanodides has been given. These salts are usually colourless, and most of them are soluble in alcohol. Its most striking property is the blood-red colour which it strikes with salts of peroxide of iron. This colour is so intense

that peroxide of iron is capable of detecting a very minute quantity of this acid.

Hydrosulphocyanic acid when left to itself undergoes gradual decomposition; a brown liquid being formed, while a yellow matter precipitates. Chlorine decomposes it, producing the same yellow matter and hydrocyanic acid. When decomposed by the galvanic battery, hydrogen is evolved at the negative pole, while cyanogen and the yellow matter appear at the positive pole.

This acid was decomposed in a very ingenious manner by Mr. Porrett,\* and his experiments have been confirmed by those of Berzelius.+ The constituents are

Composition.

1 atom hydrogen	•		0.125
2 atoms sulphur		•	4.000
l atom cyanogen	•	•	3.250
	•		
			7.375

So that its atomic weight is 7.375.

There can be no doubt that the compounds which it forms with the bases are destitute of hydrogen, and that the bases are in the metallic state. These compounds, therefore, constitute in fact sulphocyanodides. Hence hydrosulphocyanic acid must be a compound of

1 atom sulphocyano	gen	•	•	7.25
1 atom hydrogen	•	•	•	0.125
				7.075

Sulphocyanogen then must be the radical of this acid, and it is obvious that it must be a compound of

2 atoms sulphur	•	•	•	4
l atom cyanogen	•	•	•	3.25

7.25

Sulphocyanogen. From the experiments of Wöhler compared to those of Liebig, there is reason to believe that the yellow matter which makes its appearance when the acid is decomposed by galvanism, constitutes this radical. Liebig obtained it by mixing together one part of a concentrated solution of sulphocyanodide of potassium, 3 parts of water, and from 2 to  $2\frac{1}{2}$  parts of nitric acid of the specific gravity 1.42. This mixture soon deposites a good

<sup>\*</sup> Annals of Philosophy, xiii. 105.

<sup>†</sup> Kong. Vetens. Acad. Handl. 1820, p. 89.

<sup>‡</sup> Ann. de Chim. et de Phys. xli. 190.

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deal of nitrate of potash. If the liquid be decanted off these crystals, and gently heated, it speedily effervesces with violence, deutoxide of azote, carbonic acid gas, cyanogen, and hydrocyanic acid are exhaled, and the yellow matter is deposited in flocks. A current of chlorine passed through the hot solution of sulphocyanodide of potassium causes the precipitation of a great deal of the yellow matter.

This yellow matter when dried diminishes very much in bulk. It feels soft, and colours the skin with great intensity. It retains water with great obstinacy. Wöhler considers this yellow matter as a hydrosulphocyanogen; but I think that the experiments of Liebig have shown that it contains no hydrogen. From the analysis of it by this last chemist, I have no doubt that it is a compound of 2 atoms sulphur and 1 atom cyanogen. It must therefore be the radical of hydrosulphocyanic acid.

Sulphocyanogen is insoluble in water and alcohol. It may be sublimed when anhydrous (at least the greatest part of it) without undergoing decomposition. Nitric acid decomposes it, sulphuric acid, carbonic acid, and ammonia, being produced. Sulphuric acid dissolves it without alteration, and water again precipitates it from the solution. A solution of caustic potash does not dissolve it, but it changes its colour to red, and if we decant off the alkaline solution, alcohol dissolves about one-half of the red matter. What remains undissolved has a yellow colour. Liebig considers it as a sulphocyanogen containing a greater quantity of sulphur. By Liebig's analysis the composition of this yellow matter is

Cyanogen . . 3.25 Sulphur 4.111

The slight excess of sulphur may, without scruple, be considered as owing to inaccuracies in the analysis.

# SECTION XI.—OF HYDROSULPHURETTED HYDROSULPHO-CYANIC ACID.

This double acid was discovered by M. Zeise, during his History. researches on the alterations to which bicarburet of sulphur is subjected under peculiar circumstances.\* He obtained it by the following process:

Saturate absolute alcohol with as much ammoniacal gas as it will absorb at the temperature of 50°. Mix it with 0.4 of its original volume of alcohol, and with 0.16 of that volume of

<sup>\*</sup> Ann. de Chim. et de Phys. xxvi. 74.

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bicarburet of sulphur. The mixture should be made in a phial, which ought to be completely filled with it. Let the phial be well stopped and kept in the temperature of 60°. Within about an hour and a half a salt falls in crystals. This salt is a combination of sulphuret of ammonium with bicarburet of sulphur. Filter the liquid as rapidly as possible through a cloth into another phial, which must be hermetically sealed, and after having been kept for six hours at the temperature of 60° is to be cooled down to 46°, and then plunged into a mixture of snow and salt. By this treatment another salt is obtained, which is a combination of sulphuret of ammonium with hydrosulphocyanic acid. Separate this salt, wash it with a little alcohol cooled do wn to 32, and then press it between the folds of blotting Dissolve it in three times its weight of water, and add to the solution muriatic acid or sulphuric acid, diluted with twice its weight of water. After the liquids have been well mixed, pour in at once a great quantity of water, an oily looking matter is collected at the bottom of the vessel, which is hydrosulphuretted hydrosulphocyanic acid.

This double acid is colourless; but water decomposes it so rapidly that M. Zeise could not examine its properties. When it is placed in contact with a metallic oxide, the oxide is immediately reduced to a sulphuret which combines with the hydrosulphocyanic acid. Thus it appears that hydrosulphocyanic acid, though incapable of uniting with an oxidized base, enters into combination with a sulphuretted base. If we heat the salt the hydrogen of the acid unites to the sulphur of the base, and flies off in the state of sulphuretted hydrogen gas, while a metallic sulphocyanodide remains.

This double acid is a compound of

1 atom sulphuretted hydrogen	•	•	2.125
1 atom hydrosulphocyanic acid	•	•	7.375

9.500

Its atomic weight is 9.5; and like various double acids described in the class of oxygen acids, it only saturates as much base as either of its constituents would do if in a separate state.

## SECTION XII. -- OF HYDROBISULPHOCYANIC ACID.

History.

This compound acid was discovered by M. Wöhler, and I notice it here though the investigation of it is still very incomplete, to make the reader aware of the numerous compounds into which cyanogen and sulphur enter.

When sulphocyanodide of mercury is gently heated in sulphuretted hydrogen gas, or in muriatic acid gas, it undergoes decomposition, and sulphuret or chloride of mercury is formed, together with a liquid which is deposited in the coldest part of the vessel in drops. They are at first colourless; but soon become yellow, and form small transparent crystals grouped in These crystals gradually undergo spontaneous decomposition, hydrocyanic acid being given out, and an orange yellow, opaque, substance remains, which is insoluble in water. Wöhler considers this matter as a compound of

1 atom hydrogen 4 atoms sulphur 1 atom cyanogen 3.25

11.375

But this opinion has not yet been established by analysis. It is certain at least that it contains hydrogen, and more sulphur than exists in hydrosulphocyanic acid. For when heated with potassium a combination takes place with the evolution of light, hydrogen gas is given out, and the product is a mixture of sulphur and sulphocyanodide of potassium. The radical of this acid has not yet been obtained in a separate state; but if Wöhler's opinion be correct it is doubtless a compound of

4 atoms sulphur 1 atom cyanogen . 3.25 11.25

and its atomic weight is 11.25.

### SECTION XIII. -- OF DISULPHURET OF CYANOGEN.

This is a compound discovered in 1828 by M. Lassaigne, History. and deserving to be described on account of its curious properties.\* It was obtained by the following process:

Into a small globular glass vessel some cyanodide of mercury Preparation. was put, after having been previously reduced to a fine powder, and over it was poured about half its weight of bichloride of sulphur. The vessel was then closed, and left for a fortnight exposed to the action of light. A number of small crystals were gradually deposited on the upper part of the glass. There remained at the bottom of the glass a considerable quantity of corrosive sublimate, mixed with a yellow coloured matter. The

<sup>\*</sup> Ann. de Chim. et de Phys. xxxix. 197.

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crystals were purified by mixing them with a quantity of carbonate of lime, and then subliming them. When thus purified they possessed the following properties:

Properties.

The substance is transparent and colourless, and the crystals are rhomboidal plates, similar to those of chlorate of potash. When a very minute portion was applied to the tongue, it occasioned as much pain as if a sharp instrument had been thrust into the place. The part touched became red, and continued painful for some time. It has a strong smell, somewhat similar to that of chloride of cyanogen. It is so volatile that it sublimes of its own accord in close vessels, at the ordinary temperature of the atmosphere. When exposed to the light it becomes yellow in a few weeks, and finally orange, without losing its chemical properties.

It dissolves readily in water, and is still more soluble in alcohol. The aqueous solution strongly reddens the tincture of litmus; but the alcoholic solution produces no change on litmus paper, till it has been exposed for some time to the air, when it becomes red. It appears to have the property of combining with, and neutralizing the bases, and therefore is entitled to be considered as an acid.

It is decomposed by galvanism, sulphur being deposited at the positive pole, and hydrocyanic acid at the negative pole. When potassium is placed in contact with it, a combination takes place with the evolution of heat and light, sulphuret and cyanodide of potassium being formed.

Lassaigne determined the proportion of sulphur which it contained, by uniting it to potash, and calcining the salt with six times its weight of saltpetre, in a silver crucible. The mass was saturated with nitric acid, and precipitated by muriate of barytes. He obtained as a result,

Composition.

Cyanogen	•	•	•	75.8
Sulphur	•	•	•	24.2
N		]		100.0
Now this approaches very 1 atom sulph		ariy		2
2 atoms cyan	٠.	•	6.5	
				8.5

It would appear from this that it is a compound of 1 atom of sulphur and 2 atoms of cyanogen, and that its atomic weight is 8.5.

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#### SECTION XIV. -- OF SELENIOCYANOGEN.

This compound was discovered by Berzelius, and made known to the chemical world in his paper on hydrosulphocyanic acid, already referred to.\* The process employed for forming it was the same as that which succeeds in forming hydrosulphocyanic acid, only substituting selenium for sulphur. When a mixture of selenium and anhydrous ferroprussiate of potash is heated, it fuses, and we obtain a substance soluble in water and alcohol. When we evaporate the solution we obtain crystals exactly similar to those of sulphocyanodide of potassium, of which they have exactly the taste, but they are rather more soluble in water, and deliquesce more speedily in a moist atmosphere. This salt contains neither water nor hydrogen.

But though this salt is permanent, and though, doubtless, other salts containing seleniocyanogen may be formed by double decomposition, yet Berzelius was unable to obtain the seleniocyanogen in a separate state, and far less a hydroseleniocyanic acid. When an acid was added to the saline solution, the seleniocyanogen always underwent decomposition, selenium being precipitated, and when the mixture was distilled no acid whatever came over. At the commencement of the distillation (when sulphuric acid was mixed with the solution of the salt) the liquid had a most powerful and excessively disagreeable smell; but as it possessed no acid properties, he considers this smell as proceeding from a combination of selenium and sulphur, a compound not yet known.

# SECTION XV. -- OF HYDROFERROCYANIC ACID.

The salt formerly known by the names of phlogisticated History. alkali, prussiate of potash, and ferroprussiate of potash, was discovered by Macquer, and was originally employed to detect the presence of iron in liquids. It was introduced into calico printing a good many years ago, in consequence of which it soon began to be prepared in large quantities by the chemical manufacturers in this country. The first manufactory of it was established at Campsie near Glasgow, by Charles Macintosh, Esq., where it is still prepared in large quantities and very pure. The process consists in burning the hoofs of cattle mixed with saltpetre in iron pots, lixiviating what remains after this process, and setting the liquid aside when sufficiently concentrated. Beautiful crystals of the ferroprussiate are formed in large groups.

<sup>\*</sup> Kongl. Vetens. Acad. Handl. 1820, p. 97.

Chap, L

Prussiate of potash.

This salt has a fine yellow colour, is transparent, and when held between the eye and the light it appears green. crystallized in four-sided plates with bevelled edges. suppose an octahedron composed of two four-sided pyramids applied base to base, and the apex of each truncated very deep, we shall have a pretty accurate idea of the appearance of these crystals, which are usually two or three inches in diameter, and about half an inch thick. The common base of the pyramids is a square, and the inclination of a face of one pyramid to the corresponding face of the other pyramid is about 135°. Hence the inclination at the apex of the pyramids is 45°. We see that this octahedron is much longer than the regular geometrical octahedron, the angle at the apex of which is 70° 31′ 43″ 1/2. The specific gravity of this salt is 1.833. Its taste is saline and cooling, and not disagreeable. Its structure is foliated, and it may be split into thin plates parallel to the base of the pyramids, which are tough, and may be bent without breaking. I found the solubility of this salt in water as follows:

At 54°, 100 water dissolves 27.8 of the salt.

100	•	•	•	<b>65</b> ·8
150	•	•	•	87.6
200	. •	•	•	90.6

The solubility does not much increase by any augmentation of temperature beyond 200°. It is insoluble in alcohol.

When moderately heated it gives out water, and 16.625 grains of the salt gives out 3.375 grains of water. By this process the salt is not altered. For it may be dissolved in water, and obtained again in crystals as at first. But if we expose it to a red heat the salt melts, becomes black, and acquires a strong alkaline taste. If we now dissolve it in water it leaves a quantity of ferruginous matter behind it, and we obtain, by evaporating the water, a white salt which is a cyanodide of potassium.

Its composition. Berzelius\* has shown by a set of accurate experiments that the constituents of this salt are

2 atoms potassium	Ĺ	ε	•	•	10
1 atom iron	•		•	•	3.5
3 atoms cyanogen			•	•	9.75
3 atoms water	•		•	•	3.375
					26.625

<sup>\*</sup> Kong. Votens. Acad. Handl. 1819, p. 247.

The water contains just the quantity of hydrogen necessary to convert the cyanogen into hydrocyanic acid, and the quantity of oxygen requisite to convert the potassium into potash and the iron into protoxide. We might therefore either consider the salt as a compound of

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2 atoms hydrocyanate of potash,

1 atom hydrocyanate of iron,

2 atoms cyanodide of potassium, or of

1 atom cyanodide of iron,

3 atoms water.

Nor is there any experimental means of deciding which of these views is the true one. After the salt has been deprived of its water by heat, there can be no doubt that it consists of two atoms cyanodide of potassium and one atom cyanodide of iron; and as we can restore the water again by simple solution and crystallization, it is most natural to consider the salt even when crystallized as a double cyanodide with water of crystallization.

When sulphuric acid is poured upon the ferroprussiate of Decomposition. potash in powder great heat is evolved, the salt becomes white, and when heat is applied a gas is given out abundantly. This gas smells strongly of sulphurous acid, showing that the sulphuric acid is partly decomposed. There is also formed a little ammonia. The gas which comes over is combustible and burns with a blue flame. I considered it at first as a compound of one volume carbonic oxide, and one volume hydrogen gas reduced into one volume; but a subsequent and more careful examination of it satisfied me that it was a mere mixture of carbonic oxide and azotic gas. I found its specific gravity 0.9736, and when analyzed it proved a mixture of about

3 volumes carbonic oxide,

1 volume azotic gas.

I found that by means of sulphuric acid, collecting the gas evolved, determining the quantity of iron separated, and the weight of sulphate of potash formed, ferroprussiate of potash might be analyzed with tolerable accuracy. For by this process (and estimating the water driven off by heat), I obtained from 100 grains of the salt

	Potassium		•	36
	Iron .	•	•	13.51
	Cyanogen	•	•	37.49
	Water	•	•	13.00

Chap. I.	The	true	constituents	are,
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Potassium		•	•	•	<b>37·55</b> 8
Iron		•	•	•	13.145
Cyanogen	-	•	•	•	36.621
Water				•	12.676
	-	-			

100.000

I found reason to conclude that the decomposition conducted in this way took place as follows: Let us suppose 106.5 grains of ferroprussiate mixed with sulphuric acid and heated. The constituents of the salt are the following:

8 atoms potassium		•	•	<b>40</b>
4 atoms iron	•	•	•	14
12 atoms cyanogen		•	•	<b>39</b>
12 atoms water	•	•	•	13.5
				106.5

160 grains of pure sulphuric acid, or 198 grains of the acid of commerce, were required to produce complete decomposition. But I always employed about twice that quantity.

One-fourth of the cyanogen passed over undecomposed along with the gases. The remaining cyanogen was composed of

16 atoms carbon, 8 atoms azote.

2 atoms of azote went to the formation of ammonia, for the production of which 6 atoms of water were doubtless decomposed. The 6 atoms of oxygen of this water, together with 10 atoms of oxygen from sulphuric acid, converted the 16 atoms of carbon into carbonic oxide, and the 6 atoms of azote remaining passed over with the carbonic oxide, making a mixture of

16 volumes carbonic oxide,

6 volumes azotic gas.

Twelve more atoms of the oxygen of the sulphuric acid must have gone to oxidize the potassium and the iron. And 8 atoms of sulphuric acid went to saturate the potash and 2 to saturate the ammonia.

Berzelius has shown by analysis that the salt usually distinguished by the name of ferroprussiate of barytes (which will be described in a subsequent part of this volume), is a compound of

2 atoms cyanodide of barium, 1 atom cyanodide of iron. Mr. Porrett first pointed out a method of obtaining a peculiar acid from this salt. His process was as follows:

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Dissolve the salt in cold water, and for every ten grains of it add 2.53 grains of real sulphuric acid, agitate the mixture, and set it aside for some time. The whole of the barytes and sulphuric acid precipitate in combination, and leave the acid dissolved in the water.\* This acid possesses the following characters:

It has a pale lemon-yellow colour, and is destitute of smell. Hydroferrocyanic acid. It is decomposed by a gentle heat or by exposure to a strong Hydrocyanic acid is then formed, and white prussiate of iron, which by exposure to the air quickly becomes blue. When combined with the salifiable bases it forms the salts formerly called triple prussiates. It displaces acetic acid from its combinations without the assistance of heat, and forms triple prussiates with the bases previously united to that acid. expels all acids from soluble combinations when it is capable of forming insoluble salts with the bases to which they were united.+

That this is a peculiar acid, is farther proved by what happens when a solution of triple prussiate of soda is exposed to the action of the galvanic battery. Its acid (including the iron) was deposited at the positive pole, where, in consequence probably of the decomposition of water, hydrocyanic acid was volatilized, and blue prussiate of iron deposited.

Mr. Porrett has pointed out an ingenious process for obtaining this acid in the state of crystals. It is as follows: Dissolve 58 grains of crystallized tartaric acid in alcohol, and 50 grains of ferroprussiate of potash in as little warm water as possible. Mix the two liquids. Bitartrate of potash is precipitated, and the new acid remains in solution. By spontaneous crystallization it separates in small yellow coloured cubes. I have repeated this experiment with success. The crystals of the acid are soon destroyed when left exposed to the action of light. become coated with prussian blue and lose their regular shape. The same change took place even when the acid was kept in a press excluded from the light by a wooden door, which, however, was very often opened.

The analysis of this acid would be attended with peculiar difficulty on account of the ease with which it undergoes decomposition. But there is no difficulty in deducing its constitution.

<sup>+</sup> Porrett, Phil. Trans. 1814, p. 530. \* Phil. Trans. 1814, p. 580.

trom the phenomena of its formation. Ferroprussiate of barium (abstracting the water) is a compound of

2 atoms cyanodide of barium,

1 atom cyanodide of iron.

When the barium is thrown down by sulphuric acid it is in the state of barytes. It must, therefore, have united to two atoms of oxygen obtained from the decomposition of water, the two atoms of hydrogen of which must have combined to the other constituents of the salt. The new acid, therefore, must consist of

Composition.

2 atoms hydrogen	•	•	•	0.25
3 atoms cyanogen		•	•	9.75
1 atom iron	•	•	•	3.5

Gay-Lussac,\* who first pointed out that view of its constitution, considers it as a compound of 2 atoms of hydrogen, with a radical, to which he has given the name of cyanofer, and which he considers as a compound of

l atom iron	•	•	•	3.5
3 atoms cyanogen	•	•	•	9.75
				13.25

It might, if it could be obtained in a separate state, be called a tercyanodide of iron.

Supposing the constitution of this acid to be, as Gay-Lussac conceives it, we may distinguish it by the name of hydroferrocyanic acid. But I think it conceivable that it may be nothing else than a solution of 1 atom of cyanodide of iron in 2 atoms of hydrocyanic acid.

#### SECTION XVI. -- OF AZULMIC ACID.

History

This is the name by which M. P. Boullay has distinguished the charry matter, formed by the spontaneous decomposition of cyanogen.

Properties.

It is insoluble in water and alcohol, both cold and hot. It dissolves in concentrated nitric acid, to which it communicates an aurora red colour. The solution is rendered muddy by water.

It dissolves with great facility in alkaline leys and in liquid ammonia. The solutions are similar to those of ulmate of

<sup>\*</sup> Ann. de Chim. et de Phys. xxii. 320; xxiv. 224.

potash, but a good deal more red. Acids precipitate a very Class VII. light brownish-red powder, which when dried has no brilliancy, and resembles in colour china ink. The metallic salts produce brown precipitates, and completely deprive the liquid of colour. When heat is applied azulmic acid is completely decomposed into hydrocyanate of ammonia which sublimes; and when the temperature is still farther elevated a combustible gas is obtained, which burns with a blue colour, and which has the odour of cyanogen. What remains is charcoal.

M. Boullay has endeavoured to determine the composition of this acid by analysis. He decomposed it twice, and found the ratio of the volumes of azotic gas and carbonic acid gas 2 to 5. Hence he has concluded that it is a compound of

2 atoms azote	•	•	•	3.5
5 atoms carbon	•	•	•	3.75
1 atom hydrogen	•	•	•	0.125

7.375

This would make its atomic weight 7.375.

Boullay assures us that when potash is digested with glue a quantity of azulmic acid is formed, just as ulmic acid is formed when sugar of grapes is digested with the same base. This was the reason why he gave the acid the name of azulmic, meaning probably ulmic acid containing azote.\*

I have been induced to notice the opinions of Boullay on this subject, though he has not succeeded in demonstrating them by satisfactory experiments, because I consider the subject as well entitled to the attention of chemists. **Doubtless** many other combinations and modifications of cyanogen remain still unknown, and ready to recompense the future labours of the industrious chemist.

## CLASS VII.

# SULPHUR ACIDS.

The knowledge of the acid properties of the compounds, History. which sulphur forms with the acidifiable bases, is a recent acquisition to chemistry, and for the facts at present known, we are chiefly indebted to an elaborate and excellent paper on sulphur salts, by Berzelius, in the Memoirs of the Stockholm

<sup>\*</sup> Ann. de Chim. et de Phys. xliii. 282.

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Academy of Sciences for 1825 (p. 232) and 1726 (p. 53). In that paper he has shown that most of the acidifiable bases have the property of combining with sulphur and constituting acids, while the alkalifiable bases when combined with sulphur are The sulphur alkalies have the converted into alkaline bodies. property of uniting with the sulphur acids and of forming salts, a great number of which have been examined and described in the paper just referred to. In general when a sulphur acid is placed in contact with an oxygen base, decomposition takes place; so that sulphur acids can combine only with sulphur bases. For example, what was formerly considered as hydrosulphuret of potash, is not a compound of sulphuretted hydrogen with potash, but with sulphuret of potassium. sium exists in the solution, not in the state of an oxide, but of a metal, and it is kept in that state by being combined with The salt, therefore, is a compound of

9.125

so that its atomic weight, abstracting the water of crystallization, is 9.25.

I have already, in the first volume of this work, given an account of all the known compounds of sulphur and the acidifiable and alkalifiable bases. Nothing, therefore, remains to be done except to give a list of the *sulphur acids*.

In a note in page 313 of the first volume of this work, I mentioned that I meant to call all the acid compounds of suphur and a base by the name of sulphides, while to the alkaline compounds of sulphur and a base, the old name sulphurets will be confined. It is convenient (indeed necessary) to have a means of distinguishing the acid compounds of sulphur from the alkaline, and sulphide has been chosen as analogous to oxide, chloride, bromide, iodide. The following table exhibits a list of the sulphur acids with which we are at present acquainted, together with the old names by which they were formerly distinguished, and which indeed have been most commonly applied to them in the first volume of this work.

## New Names.

Old Names.

41. Sulphide of hydrogen,

- 2. Bisulphide of carbon,
- 3. Sulphide of phosphorus,

Sulphuretted hydrogen. Bisulphuret of carbon. Sulphuret of phosphorus.

List of sulphur acids. 4. Sulphide of arsenic, Realgar. Chap, II.

Persulphuret of arsenic.

Sulphuret of tellurium.

Sulphuret of antimony.

Bisulphuret of antimony.

Persulphuret of antimony.

Tersulphuret of tungsten.

Sulphuret of chromium.

Sulphuret of columbium.

Tersulphuret of molybdenum.

Quatersulphuret of molybde-

Orpiment.

5. Sesquisulphide of arsenic,

6. Persulphide of arsenic,

7. Sulphide of tellurium,

8. Sesquisulphide mony,

9. Bisulphide of antimony,

10. Persulphide of antimony,

11. Tersulphide of tungsten,

12. Tersulphide of molybdenum,

13. Quatersulphide of molybdenum,

14. Sulphide of chromium?

15. Sulphide of columbium,

16. Bisulphide of tin,

Mosaic gold.

num.

17. Probably the sulphides of the noble metals.

The salts into which these different sulphur acids enter will occupy our attention in a subsequent part of this volume.

As for the 8th and 9th classes of acids, the selenium acids and tellurium acids, the scarcity of selenium and tellurium has hitherto precluded the possibility of investigating them. of these bodies unites with hydrogen, and forms with it a compound having acid properties, namely, selenietted hydrogen, and tellurtted hydrogen. But even the salts which these two acids form have been but superficially examined. Here, then, in the present state of our knowledge, must terminate our account of the acids.

# CHAP. II.

### OF ALKALIES.

THE alkalies consist of the simple bodies described in the third chapter of the first volume of this work, under the name of simple alkalifiable bases,\* united either to oxygen, chlorine, bromine, iodine, and fluorine, sulphur, selenium, &c. are, therefore, as many classes of alkalies as there are of acids.

\* Several of the acidifiable bases have also the property of forming alkalies, when united to a small quantity of oxygen, and perhaps also of the other supporters.

#### Chap. II.

Besides these different classes, of what may be called alkalies with simple bases, there is an alkali composed of two acidifiable bases joined together, namely ammonia, which is a compound of azote These two bodies are both electro-positive, as and hydrogen. is the case with the alkaline bases; we need not therefore be surprised at their constituting an alkali when combined. Yet at present we are not acquainted with any two other electropositive bodies which constitute an alkali. But there are about 20 compound vegetable bodies which possess alkaline properties, consisting probably of carbon, hydrogen, azote, and a little oxygen united together. These may be called compound or complex alkaline bodies, in contradistinction to the alkalies with simple bases. Though only 20 are known at present, there cannot be a doubt that as the knowledge of the vegetable kingdom increases the number will greatly augment, and will probably bear some ratio to the oxygen acids with compound bases, which at present amount to 57.

Having described the properties of all the known alkalies with simple bases in the first volume of this work, I shall satisfy myself here with giving a table of the oxygen alkalies with a simple base.

Table of simple oxygen alkalies.

- 1. Potash,
- 2. Soda,
- 3. Lithia,
- 4. Barytes,
- 5. Strontian,
- 6. Lime,
- 7. Magnesia,
- 8. Alumina,
- 9. Glucina,
- 10. Yttria,
- 11. Protoxide of cerium,
- 12. Peroxide of cerium,
- 13. Zirconia,
- 14. Thorina,
- 15. Protoxide of iron,
- 16. Peroxide of iron,
- 17. Protoxide of manganese,
- 18. Sesquoxide of manganese,
- 19. Protoxide of nickel,
- 20. Protoxide of cobalt,
- 21. Oxide of zinc,
- 22. Oxide of cadmium,

- 23. Protoxide of lead,
- 24. Protoxide of tin,
- 25. Peroxide of tin,
- 26. Oxide of bismuth,
- 27. Suboxide of copper,
- 28. Oxide of copper,
- 29 Suboxide of mercury,
- 30. Oxide of mercury,
- 31. Oxide of silver,
- 32. Oxide of arsenic?
- 33. Protoxide of antimony,
- 34. Oxide of tellurium,
- 35. Oxide of chromium,
- 36. Protoxide of uranium,
- 37. Peroxide of uranium,38. Protoxide of molybdenum,
- 39. Deutoxide of molybde-
- 40. Protoxide of tungsten,
- 41. Deutoxide of tungsten,
- 42. Oxide of titanium,
- 43. Oxide of columbium.

Chap. II.

Compound alkalies.

It is unnecessary to give a table of the chlorine, bromine, &c. alkalies with a simple base, because they are the same as the preceding, substituting the terms chlorides, bromides, iodides, sulphurets, seleniets, tellurets, respectively, instead of oxides.

Ammonia may perhaps also be considered as an alkali with a simple base, if we consider azote as that base, and hydrogen as the electro-positive body with which it is in combination. It might, if a new name were wanted, be denominated a terhydrate of azote.

The following table exhibits the names and the composition of the 20 complex alkaline bodies, so far as they have been subjected to analysis.

### Constituents in atoms.

		Carbon.		Hydrog.		Azote.		Oxygen.
1. Quinin	•	60		30	•	3	•	6
2. Cinchonin		80	•	40	•	4	•	6
3. Brucin		48	•	<b>24</b>		2		6
4. Strychnin	•	60		30		3		4
5. Veratrin	•	30		24		1		6
6. Emetin		30		24		1		8
7. Cathartin								
8. Morphin	•	60		40		2		10
9. Narcotin	•	20		10		1		4
10. Caffeïn	•	5		3		l		${f 2}$
11. Delphinin								
12. Picrotoxin								
13. Solanin								
14. Daphnin								
15. Digitalin								
16. Belladonin								
17. Atropin								
18. Jalappin								
19. Smilacin								

As none of these compound alkalies has hitherto been introduced into chemistry as a reagent, I conceive that it will be better not to describe them here, but to delay the account of them till we come to treat of the vegetable kingdom. This will leave more space for an account of the salts—a class of bodies which constitute perhaps the most important department of elementary chemistry.

20. Rheïn.

The alkalies composed of the electro-positive bodies united

to chlorine, bromine, iodine, sulphur, selenium, &c., have already been described, so far as they are known, in the first volume of this work—and the salts which they form with their respective acids will come under our review hereafter. I may here close this chapter that we may enter upon an examination of the neutral compounds, which will occupy our attention in the next chapter.

### CHAP. III.

#### OF NEUTRAL COMPOUNDS.

I MIGHT in this chapter describe a considerable proportion of the vegetable and animal principles; for many of the most important of these principles neither possess the characters of acids or alkalies, at least so far as hitherto observed. But I shall confine myself in this place to those principles which are useful as chemical reagents, and which therefore it is of importance for the student to be acquainted with before he turns his attention to vegetable or animal chemistry. These neutral substances naturally arrange themselves under seven different heads. I shall, therefore, divide this chapter into the seven following sections:

1. Water,

5. Volatile oils,

2. Spirits,

6. Fixed oils,

3. Ether.

7. Bitumens.

4. Ethal,

### SECTION I .- OF WATER.

I have already, in the first volume of this work (p. 103), described the physical properties of water, and given an account of its composition. It remains only in this place to make a few observations upon it as a chemical body.

Dissolves bodies. 1. It has the property of dissolving and combining with almost all the acids, and with several of the alkaline bodies; and as it shows an equal disposition to combine with either, and does not destroy nor conceal their acid and alkaline qualities, it is obvious that it is a neutral body. It has the property also of dissolving a considerable number of the salts, which are compounds of an acid and a base. The quantity of each of these bodies which water can dissolve has a limit, and it is very various with respect to different salts. When the water has

dissolved as much of any salt as it can take up, we say that it is saturated with the salt. If we add more of the salt after it is thus saturated, it will remain at the bottom of the liquid undissolved. Or if we cause it to dissolve by increasing the temperature of the water, it is again deposited in crystals when the liquid is allowed to cool.

It is obvious that the power which thus limits the solvent property of water is the attraction which exists between the particles of the salt. When a salt is dissolved in water its particles must be equally dispersed through every part of the They must of course be arranged in regular rank and file, and the greater the quantity dissolved the smaller must the distance be between every two particles of the salt. would appear that the greater the number of particles of salt which are dissolved by the water, the smaller is the force by which the salt and water are united.\*

This may be understood by considering the particle of salt Nature of solution. to be surrounded by a certain number of particles of water, each of which is attracted to it, and the aggregate attractions of which will represent the force, by means of which the particle of salt is kept suspended in the liquid. Thus at the temperature of 58° · 25, 100 parts of water are capable of dissolving 7.74 parts of anhydrous carbonate of soda. The atomic weight of anhydrous carbonate of soda being 6.75, and that of water 1.125. It is obvious that every integrant particle of the salt must be united to about 88 integrant particles of water. We may consider every particle of the salt as surrounded by 88 particles of water, each of which attracts it to itself by a certain unknown force; so that the whole liquid may be considered as composed of small spheres, each of which has a particle of salt in the centre, while the rest of the sphere is composed of 88 particles Let us suppose now that by means of heat we can enable the 100 parts of water to dissolve an additional 7.74 parts of anhydrous salt. It is clear that the compound will now consist of 1 atom salt united to only 44 atoms water: the number of atoms of water united to the atom of salt will now be reduced to one-half the former number. The spheres will be smaller, and consequently the particles of salt nearer each other than in the former case. When the solution cools the particles of salt being combined with only half the atoms of water, and being nearer each other, a certain number of them?

<sup>\*</sup> See the experiments related with another object in view, in my treatine On Heat and Electricity, p. 197.

unite and form crystals, which in consequence of their weight, are gradually deposited at the bottom of the liquid.

What increases this tendency to crystallize is, that the crystal formed is not anhydrous, but a combination of 1 atom of salt and 10 atoms water. It would appear that the combination between these 10 atoms and the atom of salt is more intimate than that which subsists between the salt and the water in which it is dissolved. For when it combines with the salt so as to constitute a crystal, it gives out the 140° of heat which constitute the latent heat of water. Suppose the solution that is made by heat to be an aggregate of 16 sphericles, consisting each of 1 atom of anhydrous salt surrounded by 44 atoms of water. When the solution cools, 9 atoms of the salt uniting with 90 atoms of water will crystallize, and there will remain 7 atoms of salt and 704 — 90 = 614 atoms water, which will constitute very nearly the saturated solution, consisting of 1 atom salt enclosed in 88 atoms water. But the reader will form a better idea of what really takes place in such cases, if we refer to a real experiment. I dissolved 480 grains of anhydrous carbonate of soda in 2025.6 grains of hot water, and putting the solution into a well stopped phial, set it aside till it cooled. The solution remained quite liquid at the temperature of 50°; but upon drawing the cork a quantity of crystals fell, and the temperature rose to 64°. The crystals weighed 328.4 grains, equivalent to 123.15 grains of anhydrous salt. Now the atomic equivalents for these weights are as follows. The hot solution was a compound of 71·11 atoms anhydrous salt, and 1800·5 atoms of water. The crystals deposited consisted of 18-24 atoms salt, in combination with 182.4 atoms water. Of course there remained in solution 52.87 atoms of anhydrous salt combined with 1618.1 atoms of water.

The hot solution consisted of a congeries of sphericles consisting each of an atom of anhydrous salt, surrounded by  $25 \cdot 32$  atoms of water. About  $\frac{1}{4}$ th of the anhydrous salt was deposited in crystals when the cork was drawn, each atom of which carried along with it 10 atoms of water. So that there remained a solution consisting of sphericles, in the centre of each of which is an atom of salt surrounded by 30 atoms of water, which represents the solubility of the salt at  $64^{\circ}$ .

Water not only dissolves many salts and other bodies; but it has the property of entering into combination with a great many bodies in a solid state, constituting compounds, to which the name of hydrates was given by Proust; and this

name, though in some respects exceptionable, has been universally adopted by chemists. There are few or none of the simple bodies which are capable of forming hydrates with water. supporters of combustion are soluble in it to a trifling extent; and the same remark applies to hydrogen and azote; but none of the other bases, whether acid or alkaline, are capable of uniting Most of the acids are capable of forming hydrates. Such hydrates are usually called crystals of the acid; sometimes they are in the state of powders; or sometimes they constitute jellies. Most of the alkaline bases in like manner constitute hydrates, some of them in crystals; but a much greater proportion in the state of dry powders. I have already in the preceding part of this work given an account of all of these hydrates hitherto examined. No farther observations, therefore, seem requisite here.

### SECTION II .-- OF ARDENT SPIRITS.

The term ardent spirits in this country, is usually applied to the liquid obtained by distillation from different fermented liquors; all of which, as has been long known, are nothing else than alcohol more or less diluted with water, and flavoured by means of some volatile oil or other. But of late years two distinct species of liquid have been discovered, bearing a much species. closer resemblance to alcohol than to any other body whatever, though at the same time so different, that they must be considered apart. These are pyroacetic and pyroxylic spirits. shall therefore subdivide this section into three parts; in the first of which I will give an account of alcohol, in the second of pyroacetic spirit, and in the third of pyroxylic spirit.

### I. Alcohol.

Fermented liquors are of two kinds. They either consist of History. the expressed juices of various kinds of fruit, as grapes, currants, apples, &c. These juices when fermented, are known by the name of wine. Or they consist of the hot infusion of various kinds of corn, as barley, rye, rice, wheat, &c. These infusions, when fermented, are known by the names of beer and ale. Both of these kinds of liquors were known at a very early period. The Scripture informs us that Noah planted a vineyard and drank wine; and the heathen writers are unanimous in ascribing the invention of this liquor to their earliest kings and heroes. Beer, too, seems to have been discovered at a very remote period. It was in common use in Egypt during

Tacitus informs us that it was the Chap. III. the time of Herodotus.\* drink of the Germans.+ Whether the ancients had any method of procuring ardent spirits from these or any other liquors does not appear. The Greeks and Romans seem to have been ignorant of ardent spirits altogether, at least we can discover no traces of any such liquor in their writings: but among the northern nations of Europe, intoxicating liquors were in use from the earliest ages. Whether these liquors resembled the beer of the Germans we do not know.

> At what period these liquors were first subjected to distillation is unknown; though it can scarcely have preceded the time of the alchymists. The process is simple. Nothing more is absolutely necessary than to boil them in a still. portion of what comes over is ardent spirits. It is certain, at least, that the method of procuring ardent spirits by distillation was known in the dark ages; and it is more than probable that it was practised in the north of Europe much earlier. They are mentioned expressly by Thaddæus, Villanovanus, and Lully.‡

> It is by the distillation of fermented liquors that ardent spirits are obtained; and they receive various names according to the nature of the substance employed. Thus brandy is procured from wine, rum from the fermented juice of the sugarcane, whisky and gin from the fermented infusion of malt or Now ardent spirits, whatever be their name, consist almost entirely of three ingredients: namely, water, pure spirit or alcohol, and a little oil or resin, to which they owe their flavour and colour.

Rectification.

1. When these spirituous liquors are redistilled, the first portion that comes over is a fine light transparent liquid, known in commerce by the name of rectified spirits, and commonly sold under the denomination of alcohol or spirit of wine. is not, however, as strong as possible, still containing a considerable portion of water.

The method usually practised to get rid of this water is to mix the spirits with a quantity of very dry and warm salt of tartar.§ This salt has a strong attraction for water, and the greatest part of it is insoluble in alcohol. It accordingly combines with the water of the spirit; and the solution thus formed sinks to the bottom of the vessel, and the alcohol, which is lighter, swims over it, and may easily be decanted off; or, what

<sup>\*</sup> Lib. ii. n. 77.

<sup>#</sup> Bergman, iv. art. ii. 4.

<sup>+</sup> De Morib. Germ. ch. xxiii.

<sup>§</sup> Impure carbonate of potash.

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is perhaps better, the solution of potash may be drawn off from below it by means of a stopcock placed at the bottom of the vessel.\* The alcohol, thus obtained, often contains a little potash dissolved, which may be separated by distilling it in a water The spirit passes over, and leaves the potash behind. It is proper not to distil to dryness. This process is first mentioned by Lully. The liquid procured by means of it has been usually distinguished by the name of alcohol.

Alcohol is said to have been first accurately described by Arnold de Villa Nova, who was born about the end of the thirteenth century. This chemist, who was professor of medicine at Montpelier, first formed tinctures, and introduced them into medicine.†

The specific gravity of spirits, as highly rectified as possible by repeated distillations, seems to be about 0.820, at the temperature of 60°; but the alcohol of commerce, which is nothing else than rectified spirits, is seldom under .8371. By means of salt of tartar Muschenbroeck brought it as low as .815; but, in general, the alcohol concentrated by that process is not under ·821, owing to the weakness of the spirits employed. Even at the specific gravity .815 the alcohol is by no means pure, still containing a considerable portion of water. Dr. Black, by repeated distillations off muriate of lime, obtained it as low as ·800; but it was Lowitz of Petersburgh who first hit upon a method of obtaining alcohol in a state of absolute purity, or at least very nearly so. His process was published in 1796;‡ and the same year Richter made known another, by which the same purification was accomplished with still greater facility.§

The process of Lowitz is as follows: Take a quantity of fixed Method of alkali perfectly dry, and still warm, and nearly fill with it a the water. retort. Upon this pour such a quantity of alcohol (previously brought to 821 by means of salt of tartar) as can be absorbed by the alkali completely, so that the whole shall have the appearance of a solid mass without any alcohol swimming above. general, the portion ought to be two parts alkali and one part Allow this mixture to remain for 24 hours, and then alcohol.

<sup>\*</sup> See this process described by Hoffman as new, in his Observationes. Phys.-Chim. Select. p. 36, published in 1722.

<sup>+</sup> He is said also to have been the first who obtained the oil of turpentine. He procured it by distilling turpentine, and employed it as a solvent of resins. I have not been able to find any traces of these discoveries in any of the tracts of Arnold that I have looked through.

<sup>‡</sup> Crell's Annals, 1796, i. 195.

<sup>§</sup> Ibid. ii. 211.

I presume in the state of carbonate.

Chap III. distil by a heat so moderate, that about two seconds elapse between the falling of the drops of alcohol from the beak of the receiver. When this interval increases, the receiver must be changed; for it is a sign that all the strong alcohol has come over. What comes over next is weaker. By this process Lowitz obtained alcohol of the specific gravity 0.791 at the temperature of 68°.

> When Richter repeated the experiment of Lowitz, he reduced the alcohol to the specific gravity 0.792 at the temperature of 68°, but could not bring it any lower. He found, upon trial, that the following method, which is much more expeditious, answered equally well with that of Lowitz: he exposed a quantity of the salt called chloride of calcium to a red heat, reduced it to powder, and introduced it while yet warm into a retort, and poured over it at intervals a quantity of alcohol, of 0.821, nearly equal to it in weight. A violent heat was produced. The retort was put upon a sand-bath, a receiver adjusted, and the liquid made to boil. The salt was dissolved, and formed with the alcohol a thick solution. The portion that had passed over into the receiver was now poured back, and the distillation was continued till one-half of the alcohol came over into the receiver. The receiver must now be changed, and the distillation continued; because what comes over next is weaker. The first portion of alcohol thus obtained was of the specific gravity 0.792, at the temperature of 68°.

Another method.

M. Pajot des Charmes has suggested another mode of rectifying spirits, founded upon the property which deliquescent salts, as chloride of calcium, chloride of manganese, &c. have of absorbing the vapour of water, without acting upon the vapour of alcohol. He puts into a flat vessel the spirits which he wishes to rectify. And in another vessel standing on a tripod over the spirits, he puts a quantity of dry chloride of calcium reduced to a coarse powder, and covers the whole with a large glass receiver, placed inverted over a flat dish containing enough of mercury or melted tallow, to exclude effectually all communication between the external air and the inside of the receiver. The spirits being a compound of alcohol and water, both of which liquids evaporate at the common temperature of the atmosphere, the receiver is soon filled with the vapours of each. But the chloride of calcium absorbing the vapour of water as fast as it is formed, the aqueous portion of the liquid continues to evaporate; while the alcohol vapours not being absorbed, continue to fill the receiver, and by their elasticity

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prevent all farther evaporation of that liquid. This process being continued for several days, the spirits obviously must become stronger. When the chloride of calcium begins to appear moist on the surface, the process must be stopped. Suppose the specific gravity of the spirits at first 0.920 by this first process, the specific gravity will probably be reduced as low as 0.890. Remove the first portion of chloride of calcium, and repeat the process with a fresh portion. By repeating the process two or three times, the specific gravity of the spirits may be easily reduced to 6.817.\*

Mr. Thomas Graham of Glasgow has considerably improved this process, by substituting quicklime for chloride of calcium, and by putting the alcohol and lime under the exhausted receiver of an air-pump. This increases the rapidity of the process, and probably occasions a greater increase in the strength of the alcohol. Indeed, he was able in this way to produce absolute alcohol. This mode of rectifying spirits might probably be employed with advantage by the rectifier. The loss of alcohol would not be great, and the lime though slacked would not be in the least injured in its properties; but might be applied again and again to the same purpose, by simple exposure to a red heat.

- 2. Alcohol obtained by these processes is a transparent liquor, properties. colourless as water, of a pleasant smell, and a strong penetrating agreeable taste. When swallowed it produces intoxication. Its properties differ somewhat according to its strength. When procured by Lowitz's or Richter's process, we may distinguish it by the name of pure alcohol, or absolute alcohol, as no method known can deprive it of any more water. When the specific gravity is higher, the alcohol is contaminated with water, and the proportion of that liquid present increases with the specific gravity. Chemists, in general, have employed this impure alcohol, or this mixture of alcohol and water, in their experiments; and as they have too often neglected to point out the specific gravity of the spirit used, we are still in some measure ignorant of the properties of this important liquid.
  - \* Ann. de Chim. et de Phys. xxix. 328.
- † Edinburgh Phil. Trans. xi. 175. Mr. Graham found that chloride of calcium could not be used without considerable loss of the alcohol, because it absorbs alcoholic vapour as well as aqueous. The same remark applies to sulphuric acid, which therefore would not answer for concentrating alcohol.
- ‡ Fahrenheit was one of the first who ascertained some of the remarkable properties of alcohol with exactness. His alcohol was of the specific gra-

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8. Alcohol is perfectly limpid and remarkably fluid, and it may be exposed to a lower temperature than any other known substance without losing its fluidity. Mr. Walker of Oxford reduced an alcohol thermometer to the temperature of — 91° without producing any change in it. But Mr. Hutton of Edinburgh announced in 1813, that he had been able to freeze it by exposing it to a cold of — 110°. The alcohol employed by him was of the specific gravity 0.798 at the temperature of 60°. He says that the alcohol divided into three layers. The uppermost was yellow, the undermost was alcohol. What the middle one was he does not say.\* But as Mr. Hutton has thought proper to conceal the method which he employed, and as no one else has been able to produce so great a degree of cold, the freezing of alcohol must still be considered as doubtful.

It is a very volatile liquid. Fahrenheit found that alcohol of the specific gravity of about  $\cdot 820$ , at the temperature of 60°, boiled when heated to  $176^{\circ}$ . When of the specific gravity  $\cdot 800$  it boils at  $173^{\circ}\frac{1}{6}$ .

The following table exhibits the boiling point of alcohol of various strengths, as determined by the experiments of Yelin.

Alcohol per cent.	Sp. gravity of alcohol at 68°.	Boiling point.	Alcohol per cent.	Sp. gravity of alcohol,	Boiling point,
100 99 98 97	0·796 0·794 0·797 0·800	170°.6 170·42 170·33 170·33	96 95 94	0·803 0·805 0·808	170°·46 170.58 170·55

I have inserted these results of Yelin (though satisfied that he places the boiling point too low) to draw the attention of experimenters to the variations which he observed in the boiling

vity '825 at the temperature of 48°. See Phil. Trans. 1724, vol. xxxiii. p. 114. Fourcroy informs us that the specific gravity of the most highly rectified alcohol is 0'8293, without specifying the temperature. The extremity of Baumé's hydrometer for spirits, (according to Nicholson's table, Quarto Jour. i. 39), answers to the specific gravity '817, temp. 55°. This may be considered as beyond the strength of the alcohol used. In Germany, before Lowitz's experiments, the strongest alcohol seems seldom to have exceeded 0.821 at 68°; and in this country it is commonly considerably weaker. The highest point of Clark's hydrometer corresponds with alcohol of about '834 at 30°. Dr. Lewis states the purest alcohol of the specific gravity 0.820.—Neuman's Chem.

<sup>4\*</sup> Annals of Philosophy, i. 221. + Phil. Trans. 1724, vol. xxxiii. p. 1.

<sup>‡</sup> Kastner's Arch. ii. 340.

point, at very small changes in the strength. He found that alcohol of 0.800 had the lowest boiling point, and that alcohol of 0.791 required a higher temperature to boil it. I am persuaded that these results of Yelin are inaccurate, and that the following table, furnished by Gröning,\* comes nearer the truth, at least it agrees much better with my own trials.

Alcohol per cent.	Sp. gravity at 68°.	Boiling point,	Alcohol per cent.	Sp. gravity at 68°.	Boiling point.
5	0.994	205-34	55	0.903	179.096
10	0.987	199-22	60	0.892	179-42
15	0.980	195.8	65	0.880	178.7
20	0.973	192.38	70	0.868	177.62
25	0.965	189.5	75	0.856	176.54
30	0.956	187-16	80	0.844	175.46
35	0.946	185	85	0.831	174.92
40	0.936	183.38	90	0.818	174.2
45	0.925	182-12	95	0.805	173.12
50	0.914	181.58			İ

Beiling points.

Boiling converts alcohol into an elastic fluid capable of resisting the pressure of the atmosphere as long as the heat continues, without undergoing any change, but again condensed into alcohol when the temperature is reduced. Its specific gravity, according to the experiments of Gay-Lussac, is 1.6133.+ believe the true specific gravity to be 1.6000.

4. Alcohol has a strong affinity for water, and is miscible Combines with water. with it in every proportion. The specific gravity varies according to the proportion of the two liquids combined; but, as happens in almost all combinations, the specific gravity is always greater than the mean of the two liquids; consequently there is a mutual penetration: and as this penetration or condensation varies also with the proportions, it is evident that the specific gravity of different mixtures of alcohol and water can only be ascertained by experiment. As the spirituous liquors of commerce are merely mixtures of alcohol and water in different proportions, and as their strength can only be ascertained with precision by means of their specific gravity, it becomes a point of very great importance to determine with precision the proportion of alcohol contained in a spirit of a given specific gravity: and as the specific gravity varies with the temperature it is necessary to make an allowance for that likewise.

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The importance of knowing with precision the proportion of alcohol contained in spirits of every specific gravity, has induced many different persons to make experiments in order to ascertain this point with exactness; but as they set out from alcohol of very different strengths, it is not easy to compare their results with each other. We have seen that the pure alcohol, by Lowitz' process, is of the specific gravity .791 at the temperature of 68°. That chemist mixed various proportions of this alcohol with given weights of pure water, and after allowing the mixtures to remain for 24 hours, took the specific gravity of each at the temperature of 68°. The following table exhibits the result of these experiments. The first two columns contain the proportion of alcohol and water (in weight) mixed together, and the third the specific gravity of the mixture at 680. I have added a fourth column, containing the specific gravity at 60°, the temperature commonly preferred in this country.\*

Specific gravity of various mixtures of alcohol and water,

100 pa	rts.	Sp. gr	avity.	100 I	arts.	Sp. G	ravity.
Alcohol.	Wat.	At 68°.	At 60°.	Alcoh.	Wat,	at 68°.	at 60°.
100		791	796	79	21	847	851
99	1	794	798	78	22	849	853
98	2	797	801	77	23	851	855
97	3	800	804	76	24	853	857
96	4	803	807	75	25	856	860
95	5	805	809	74	26	859	863
94	6	808	812	73	27	861	865
93	7	811	815	72	28	863	867
92	8	813	817	71	29	866	870
91	9	816	820	70	30	868	871
90	10	818	822	69	31	870	874
89	11	821	825	68	32	872	875
88	12	823	827	67	33	875	879
87	13	826	830	66	34	877	880
86	14	828	832	65	35	880	883
<b>85</b>	15	831	835	64	36	882	886
84	16	834	838	63	37	885	889
83	17	836	840	62	38	887	891
82	18	839	843	61	39	889	893
81	19	842	846	60	40	892	896
80	20	844	848	59	41	894	898

<sup>\*</sup> Crell's Annals, 1796, i. 202.

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100 1	Parts.	Sp. Gi	avity.	100	Parts.	<b>8p.</b> G:	ravity.
Alcoh.	Wat.	at 68°.	at 60°.	Alcoh.	Wat.	at 68°.	at 60°.
58	42	896	900	28	72	959	962
57	43	899	903	27	73	961	963
56	44	901	904	26	74	963	965
55	45	903	906	25	75	965	967
54	46	905	908	24	76	966	968
53	47	907	910	23	77	968	970
52	48	909	912	22	78	970	972
51	49	912	915	21	79	971	973
50	50	914	917	20	80	973	974
49	51	917	920	19	81	974	975
48	52	919	922	18	82	976	1
47	<b>53</b> .	921	924	17	83	977	
46	54	923	926	16	84	978	
45	55	925	928	15	85	980	1
44	56	927	930	14	86	981	
43	57	930	933	13	87	983	
42	58	932	935	12	88	985	
41	59	934	937	11	89	986	
40	60	936	939	10	90	987	]
39	61	938	941	9	91	988	
38	62	940	943	8	92	989	
37	63	942	945	7	93	991	
36	64	944	947	6	94	992	1
35	65	946	949	5	95	994	
34	66	948	951	4	96	995	
<b>3</b> 3	67	950	953	3	97	997	
32	68	952	955	2	98	998	
31	69	954	957	1	99	999	
30	70	956	958		100	1000	
29	71	957	960			1	1

Mr. Tralles of the Berlin Academy published an elaborate set of experiments upon this subject in the year 1811.\* The following table which exhibits the result of his experiments, I consider as deserving to be generally known, though, as he used volumes instead of weights, his experiments cannot be expected to possess the accuracy of those of Mr. Gilpin, which I shall give afterwards.

<sup>#</sup> Gilbert's Annalen, xxxviii. 369.

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100 measures contain of, alcohol,	Sp. gravity at 60°.	Differences	100 measures contain of alcohol.	Sp. gravity at 60°.	Differences.
0	0.9991		43	0.9461	17
1	0.9976	15	44	0.9444	17
2	0.9961	15	45	0.9427	17
3	0.9947	14	46	0.9409	18
4	0.9933	14	47	0.9391	18
5	0.9919	14	48	0.9373	18
6	0.9906	13	49	0.9354	19
7	0.9893	13	<b>5</b> 0	0.9335	19
8	0.9881	12	51	0.9315	20
9	0.9869	12	52	0.9295	20
10	0.9857	12	53	0.9275	20
11	0.9845	12	54	0.9254	21
12	0.9834	11	55	0.9234	20
13	0.9823	11	56	0.9213	21
14	0.9812	11	57	0.9192	22
15	0.9802	10	58	0.9170	22
16	0.9791	11	59	0.9148	22
17	0.9781	10	60	0.9126	22
18	0.9771	10	61	0.9104	22
19	0.9761	10	62	0.9082	22
20	0.9751	10	63	0.9059	23
21	0.9741	10	64	0.9036	23
22	0.9731	10	65	0.9013	23
23	0.9720	11	66 ·	0.8989	24
24	0.9710	10	67	0.8965	24
25	0.9700	10	68	0.8941	24
26	0.9689	11	69	0.8917	24
27	0.9679	10	70	0.8892	25
28	0.9668	11	71	0.8867	25
29	0.9657	11	72	0.8842	25
30	0.9646	11	73	0.8817	25
31	0.9634	12	74	0.8791	26
32	0.9622	12	75	0.8765	26
33	0.9609	13	76	0.8739	26
34	0.9596	13	77	0.8712	27
35	0.9583	13	<b>7</b> 8	0.8685	27
36	0.9570	13	79	0.8658	27
37	0.9556	14	80	0.8631	27
38	0.9541	15	81	0.8603	28
39	0.9526	15	82	0.8575	28
40	0.9510	16	83	0.8547	28
41	0.9494	16	84	0.8518	29
42	0.9478	16	85	0.8488	30

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100 measures contain of alcohol.	Sp. gravity at 60°.	Differences.	100 measures contain of alcohol,	Sp. gravity at 60°.	Differences
86	0.8458	30	94	0.8194	36
87	0.8428	30	95	0.8157	37
88	0.8397	31	96	0.8118	39
89	0.8365	32	97	0.8077	41
90	0.8332	33	98	0.8034	43
91	0.8299	33	99	0.7988	46
92	0.8265	34	100	0.7939	49
93	0.8230	35	-		

The importance of this object, both for the purposes of revenue and commerce, induced the British Government to employ Sir Charles Blagden to institute a very minute and accurate series of experiments. An account of these was published by Blagden in the Philosophical Transactions for 1790; and a set of tables, exhibiting the result of them, was drawn up by Mr. Gilpin, who had performed the experiments, and published them in the Philosophical Transactions for 1794. The following table, extracted from these, contains the specific gravity of different mixtures of alcohol and water at every 5° of temperature from 30° to 100°. The alcohol employed as a standard was of the specific gravity 0.825 at the temperature of 60°: and was composed, according to the experiments of Mr. Gilpin, of 100 parts of alcohol of the specific gravity 0.814 and 4.5 of water. From the preceding table, we see that alcohol of .825 is composed of

89 pure alcohol

100

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Real Specific Gravities at the different Temperatures.

Heat	Pure Alcohol,	100 alcohol 5 water.	100 alcohol 10 water.	100 alcohol 15 water.	100 alcohol 20 water.	100 alcohol 25 water.	100 alcohol 30 water.	100 alcohol 35 water.	100 alcohol 40 water.	100 alcohol 45 water.
30°	-83896	-84995	-85957	86825	-87585	-88282	188921	-89511	-90054	-90558
35	83672	84769	85729	86587	87357	88059	88701	89294	89839	90345
40	83445	84539	85507	86361	87134	87838	88481	89073	89617	90127
45	83214	84310	85277	86131	86905	87613	88255	88849	89396	89909
50	82977	84076	85042	85905	92998	87384	88030	88626	89174	89684
55	82736	83834	84805	85664	86441	87150	87796	88393	88945	89458
09	82500	83599	84568	85430	86208	86918	87569	88169	88720	89232
65	82262	83362	84334	85193	85976	98998	87337	87938	88490	89006
20	82023	83124	84092	84951	85736	86451	87105	87705	88254	88773
75	81780	82878	83851	84710	85496	86212	86864	87466	88018	88538
98	81530	82631	83603	84467	85248	85966	86622	87228	87776	88301
85	81291	82396	83371	84243	85036	85757	86411	87021	87590	88120
96	81044	82150	83126	84001	84797	85518	86172	86787	87360	87889
95	80794	81900	82877	88753	84550	85272	82658	86542	87114	87654
100	80548	81657	82639	83513	84308	85031	85688	86302	86879	87421

Real Specific Gravities at the different Temperatures.

-93991	93790	93592	93382	93177	92963	92758	92546	92333	92111	16816	91729	91511	91290	99016
-93741	93541	93341	93131	92919	92707	92499	92283	92069	91849	91622	91465	91548	91029	90305
-93474	93274	93072	92859	92647	92436	92225	92010	91793	91569	91340	91186	29606	90747	90522
-93191	98676	92783	92570	92358	92145	91933	91715	91493	91270	91046	90882	89906	90443	90215
-92889	92680	92476	92264	92051	91837	91622	91400	91181	90952	90723	90558	90342	90119	88888
.92563	92355	92151	91937	91723	91502	91287	91066	90847	90617	90385	90209	88668	89763	89536
.92217	92009	91799	91584	91370	91144	90927	20706	90484	90252	90021	89843	89617	89390	89128
.91847	91640	91428	91211	26606	89406	90549	90328	90104	89872	89639	89460	89930	80003	88769
.91449	91241	91026	90812	90296	90367	90144	89920	89695	89464	89225	89043	88817	88588	88357
.91023	90811	90206	90380	90160	89933	89707	89479	89252	89018	88781	88605	88376	88146	87915
300	3 3	04	5	000	55	000	22	2	2	2	70	2 8	75	9
	.91023 .91449 .91847 .92217 .92563 .92889 .93191 .93474 .93741	•         •	•         •91023         •91449         •91847         •92217         •92563         •92889         •93191         •93474         •93741           90811         91241         91640         92009         92355         92680         92986         93274         93541           90596         91026         91428         91799         92151         92476         92783         93072         93341	-91023         -91449         -91847         -92217         -92563         -92889         -93191         -93474         -93741           90811         91241         91640         92009         92355         92680         92986         93274         93541           90596         91026         91428         91799         92151         92476         92783         93072         93341           90380         90812         91211         91584         91937         92264         92570         92859         93131	90811         91241  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   92919           89933         90367         90768         91144         91502         91837         92145         92436         92436         92436           89707         90144         90549         90927         91622         91933         92225         92499	90811         91241         91640         92217         92563         92889         93191         93474         93741           90811         91241         91640         92009         92355         92680         92986         93274         93541           90596         91026         91428         91799         92151         92476         92783         93072         93341           90380         90812         91211         91584         91937         92264         92570         92859         93131           90160         90596         90997         91370         91723         92051         92358         92647         92919           89933         90367         90768         91144         91502         91837         92145         92436         92499           89479         89920         90328         90707         91066         91400         91715         92010         91715         92010         92285         92499	-91023         -91449         -91847         -92217         -92563         -92889         -93191         -93474         -93741           90811         91241         91640         92009         92355         92680         92986         93274         93541           90596         91026         91428         91799         92151         92476         92783         93072         93341           90380         90812         91211         91584         91937         92264         92570         92859         93131           90160         90596         90997         91370         91723         92051         92358         92647         92919           89933         90367         90144         91502         91837         92145         92436         92436           89479         89920         90328         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Real Specific Gravities at the different Temperatures.

	100 alcohol 100 water.	96 alcohol 100 water.	90 alcohol 100 water,	85 alcohol 100 water.	80 alcohol 100 water.	75 alcohol 100 water.	70 alcohol 100 water.	65 alcohol 100 water.	60 alcohol 100 water.	55 alcohol 100 water.
<b>3</b> 0°	-94222	-94447	-94675	.94920	-95173	.95429	-95681	-95944	-96209	-96470
35	94025	94249	94484	94734	94988	95246	95502	95772	96048	96315
\$	93827	94058	94295	94547	94802	95060	95328	95602	95879	96159
45	93621	93860	94096	94348	94605	94871	95143	95423	95705	95993
50	93419	93658	93897	94149	94414	94683	94958	95243	95534	95831
55	93208	93452	98986	93948	94213	94486	94767	95057	95357	95662
09	93002	93247	93493	93749	94018	94296	94579	94876	95181	95493
65	92794	93040	93285	93546	93822	94099	94388	94689	95000	95318
70	92580	92828	93076	93337	93616	93898	94193	94500	94813	95139
75	92364	92613	92865	93132	93413	93695	68686	94301	94623	94957
<b>8</b>	92142	92393	92646	92917	93201	93488	93785	94102	94431	94768
82	91969								-	
06	91751								-84	
95	91531									
100	91310									

Real Specific Gravities at the different Temperatures.

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Chap. III.

Tables constructed from those furnished by Sir Charles Blagden are employed by the officers of Excise in levying the duty on spirits in this country. The business of the officer is to determine the specific gravity, and the bulk of the spirits, from which he is enabled, by means of his tables, to calculate the duty to be paid. A peculiar language has crept into use among the spirit-dealers, which it will be proper in this place to explain.

Proof spirit,

Before the means of determining the true quantity of alcohol in spirits were known, the dealers were in the habit of employhig a very rude method of forming a notion of the strength.

A given quantity of the spirits was poured upon a quantity
of gunpowder in a dish and set on fire. If at the end of the
combustion, the gunpowder continued dry enough, it took
fire and exploded; but if it had been wetted by the water in
the spirits, the flame of the alcohol went out without setting
the powder on fire. This was called the *proof*. Spirits which
kindled gunpowder were said to be above proof, those that did
not set fire to it were said to be below proof.

From this origin of the term proof, it is obvious that its meaning must have been at first very indefinite. It could serve only to point out those spirits which were too weak to kindle gunpowder, but could not give any information respecting the relative strength of those spirits which were above proof. Even the strength of proof was not fixed, because it was influenced by the quantity of spirits employed—a smaller quantity of a weaker spirit might be made to kindle gunpowder, while a greater quantity of a stronger might fail. Clarke, in his hydrometer, which was invented about the year 1730,\* fixed the strength of proof spirits on the stem at the specific gravity of 0.920 at the temperature of 60°. At last an act of parliament fixed the strength of proof spirit by enacting, that at the temperature of 51°, 13 volumes of proof spirit weighed exactly as much as 12 parts of water at the same temperature. Now if we were to raise the temperature of the water and the proof spirits from 51° to 60° (it follows from the known dilatability of each by heat that the 12 volumes of water would become 12.00479, and the 13 volumes of alcohol would become Now the specific gravity of water at 60° being reckoned unity, we will get that of proof spirit at the same temperature by dividing 12.00479 by 13.0482. The quotient

<sup>\*</sup> Phil. Trans. 1730, vol. xxxvi. p. 277.

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0.9200341 is the specific gravity of proof spirit at 60°, according to the act of parliament. Now if we refer to Mr. Lowitz's table, given in a preceding part of this section, we find that such spirits are composed of 49 parts by weight of alcohol and 51 parts of water. So that proof spirits, as determined by act of parliament, does not differ very much from a mixture of equal weights of absolute alcohol and water. But the strength of the alcohol, according to which the duty on spirits in this country is levied, being only 0.825, it is obvious that proof spirit is a mixture of 100 parts alcohol (of 0.825), and 82 parts of water by weight; or if we take the volumes of the two constituents, we have

50.16 volumes of alcohol of 0.825,

49.84 volumes of water,

so that proof spirit is very nearly a mixture of equal volumes of alcohol of 0.825 and water.

5. Neither common air nor oxygen gas has any action on Constituents of alcohol. alcohol in moderate temperatures, whether in the liquid or gaseous state; but in high temperatures the case is different. When set on fire in the open air it burns all away with a blue flame, without leaving any residuum. Boerhaave observed, that when the vapour which escapes during this combustion is collected in proper vessels, it is found to consist of nothing but Junker had made the same remark: and Dr. Black suspected from his own observations, that the quantity of water obtained, if properly collected, exceeded the weight of the alcohol consumed. This observation was confirmed by Lavoisier; who found that the water produced during the combustion of alcohol exceeded the alcohol consumed by about 4th part.\* Mr. Saussure, junior, has shown that 100 parts of alcohol when burnt yield 132 parts of water.+ A proof that it contains a considerable proportion of hydrogen as a constituent.

When the vapour of alcohol is mixed with oxygen gas in the proper proportion, the mixture detonates when presented to a lighted taper, or when fired by electricity, as a mixture of oxygen and hydrogen gases do.. This fact seems to have been first observed by Dr. Ingenhousz, or at least his experiments on ether appear to have led to it. The products of the combustion are water and carbonic acid.§

Different opinions were entertained by chemists about the

§ Cruikshank's Nicholson's Quarto Jour. v. 205.

<sup>\*</sup> Mem. Par. 1781, p. 493. + Nicholson's Journal, xxi. 263.

<sup>‡</sup> See his Experiences et Observations sur divers Objets de Phys. p. 173

Chap. III. nature of alcohol. Stahl thought that it was composed of a very light oil, united by means of an acid to a quantity of water. According to Junker, it was composed of phlogiston, combined with water by means of an acid. Cartheuser, on the other hand, affirmed that it contained no acid, and that it was nothing else than pure phlogiston and water. But these hypotheses were mere assertions supported by no proof whatever. Lavoisier was the first who attempted to analyze it. He burnt a quantity of alcohol of the specific gravity 0.8293 in a glass jar, standing over mercury and filled with oxygen gas, and he calculated the constituents of the alcohol from the quantity of oxygen gas consumed, and the quantity of carbonic acid formed by the combustion of a given weight of alcohol.\* But the results which he obtained by this process could not be accurate, because a quantity of the alcohol would evaporate without burning, and he had no means of determining the proportion which this quantity bore to the whole. In the year 1807, Mr. Theodore de Saussure resumed the investigation of the composition of alcohol. He tried the method of Lavoisier. likewise detonated a mixture of vapour of alcohol and oxygen gas by means of electricity. But the method upon which he put the greatest reliance was to decompose alcohol by passing it through a red hot porcelain tube and to analyze the combustible gas which was produced.† The results which he obtained by these different processes differed considerably from each other. They were no doubt nearer the truth than those of Lavoisier; because considerable progress had been made in the art of analysis since the time of that philosopher. But they could be considered only as approximations. M. De Saussure turned his attention to this subject again in 1813, and published a new analysis of alcohol, which may be considered as approaching as nearly to precision as the present state of the science of chemistry will admit. He employed for his analysis, alcohol of the specific gravity 0.8302 at the temperature of 62.8°, obtained by rectifying common spirits. This alcohol was a compound of 13.8 water and 86.2 of the absolute alcohol of Richter; the water being subtracted from the products obtained, the residue gave the composition of the absolute alcohol of Richter. His method of analysis was to pass the alcohol through a red-hot porcelain tube, and along a glass tube hear six feet in length surrounded with ice. All the products

<sup>\*</sup> Mem. Par. 1781.

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were carefully collected and weighed. There was a little charcoal deposited in the porcelain tube and a very little oil in the glass tube. The water condensed amounted to  $\frac{1000}{4460}$  of the weak alcohol employed, and it contained  $\frac{1000}{2810}$  of its weight of absolute alcohol. The combustible gas weighed 912.3 grains, (the weak alcohol employed was 1256.7 gr.) and there was a loss of 55.82 grains. The gas was burnt in a eudiometer with oxygen gas. The products were carbonic acid and water. For every two volumes of carbonic acid produced, three volumes of oxygen were consumed. Now this is the property of olefiant gas. Hence it follows, that the gas is precisely the same in its composition, as if it were a mixture of vapour of water and olefiant gas. The result of the analysis was, that the absolute alcohol of Richter is a compound of

Hydrogen	•	•	•	13.70
Carbon		•	•	51.98
Oxygen	•	•	•	34.32
0.41	1 .1		. 1	100.00
Or the composition may	be th	us sta	ted,	
Olefiant gas	•	•	•	61.63
Water	•	•	•	38.37
				100.00

It would apppear then that by exposing the vapour of alcohol to a strong red heat, it is converted into olefiant gas and vapour of water. If we suppose it a compound of one volume of olefiant gas and one volume of vapour of water reduced into one volume, its specific gravity in the state of vapour would be 1.5972. For

Sp. gr. of olefiant gas is	•	•	0.9722
vapour of water	•	•	0.6250

1.5972 = sp. gr. of

alcohol vapour. Now the specific gravity, as determined by Gay-Lussac, is 1.6133, which differs from the specific gravity derived from that of olefiant gas and vapour of water added together by only one per cent.

Thus alcohol (if we can confide in the analysis of Saussure), is a compound of equal volumes of olefiant gas and vapour of water, united together and condensed into a liquid. Olefiant gas contains two atoms carbon and two atoms hydrogen, while

# water is composed of one atom oxygen and one atom hydrogen. Thus the atomic constituents of alcohol are

l atom oxygen	•	•	= 1
2 atoms carbon	•	•	= 1.5
3 atoms hydrogen	•	•	= 0.375
			····
			2.875

and its atomic weight is 2.875.

The analysis of Saussure has been confirmed by MM. Dumas and Boullay, who found the constituents of absolute alcohol to be

Carbon	•	•	•	•	<b>52·37</b>
Hydrogen	•	•	•	•	13.31
Oxygen	•	•	•	•	34.61
					100.29

Now this is equivalent to

2.017 atoms carbon, 3.07 atoms hydrogen, 1 atom oxygen

constituting very near approximations to the truth.

Action of alcohol on simple bodies.

- 6. Alcohol readily dissolves bromine and iodine, and forms deep-coloured solutions, which act with considerable energy when taken into the stomach. Chlorine gas is absorbed by it in considerable quantity, the alcohol acquires a greenish colour and undergoes partial decomposition, the nature of which seems to vary with the strength of the alcohol. This at least is the most probable reason why the results of Scheele, Berthollet, and Thenard, differ so much from each other. Scheele obtained muriatic ether, Berthollet acetic acid and a sweet matter, while Thenard obtained some carbonic acid, a charry matter, &c. Vogel assures us that if a current of chlorine gas be passed through alcohol, exposed to the direct rays of the sun, combustion takes place. It is said by Bercht that if two parts of chlorate of potash, 12 parts of alcohol, and one part of sulphuric acid be distilled, acetic ether passes over into the receiver.
- 7. 100 volumes of alcohol, at the temperature of 64°, absorb, according to Saussure, 16 volumes of oxygen gas.

100 volumes of alcohol at the temperature of 64°, according to the same chemist, absorb five volumes of hydrogen gas, 42 volumes of azotic gas, 153 volumes of protoxide of azote,

<sup>\*</sup> Ann. de Chim. et de Phys. xxxvi. 297.

14.5 volumes of carbonic oxide gas, 186 volumes of carbonic acid gas, and 127 volumes of olefiant gas.

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It does not dissolve boron, but it dissolves boracic acid, and the solution burns with a green-coloured flame, which is characteristic of that acid.

One part of phosphorus dissolves in 320 cold and 240 hot alcohol of the specific gravity 0.799. The last solution lets fall a portion of the phosphorus when it cools. If the alcohol thus saturated with phosphorus be boiled, the vapour which escapes is luminous in the dark. When the alcohol is dropt into water, a lambent flame plays on the surface of the liquid.

When sulphur and alcohol are brought into contact in the state of vapour, they combine and form a reddish coloured liquid, which exhales the odour of sulphuretted hydrogen. This compound was first formed by the Count de Lauraguais, who employed the following process: Some flowers of sulphur were put into a large glass cucurbite, having a glass vessel in its centre, containing alcohol. A head was adjusted, the cucurbit placed in a sand-bath, and heat applied. The sulphur was volatilized, and the alcohol converted into vapour at once. These meeting together in the head, united and formed the red liquor wanted.\* It was supposed by chemists that sulphur cannot be dissolved in alcohol, except by a similar process;+ but from the experiments of Favre, this does not appear to be the case. ‡ He digested, during 12 hours, one part of flowers of sulphur in eight parts of alcohol, of the specific gravity 0.837, in a heat not sufficient to produce boiling. The alcohol assumed a yellow colour, and acquired the smell and taste of sulphuretted hydrogen. Another portion of the same alcohol was digested for a month, cold, on sulphur. The effect was the same. On trying alcohol of various strength from .817 to ·867, he found that the alcohol acted with more energy in proportion to its strength.

The sulphuretted alcohol prepared by Lauraguais' method contains about  $\frac{1}{66}$ th of sulphur. The sulphur is precipitated by water.

At the temperature of 64°, according to Saussure, 100 volumes of alcohol absorb 116 volumes of sulphurous acid gas, and 600 volumes of sulphuretted hydrogen gas.

<sup>\*</sup> Mem. Par. 1758, p. 9.

<sup>†</sup> See the Elements de Chymie of the Dijon Academy, iii. 287. Four-croy's Connoissances Chymiques, viii.

t Gehlen's Jour. ii. 343.

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The solubility of selenium in alcohol is unknown; but it readily dissolves selenious acid.

These are the only simple substances upon which alcohol

has any notable action.

8. I shall give an account of the action of the oxygen acids with a simple base upon alcohol in the next section. The following table exhibits the solubility of such of the oxygen acids with compound bases in alcohol as have been determined.\*

Solubility of acids in it.

€.	1 Part of	In parts	of alcohol,	Sp. gravity of alcohol.	Experimenters.
		Cold.	Hot.		
	Oxalic acid	2.5	1.8	0.830?	Bergman,
	Vinic acid	148		0.809	Walchner,
	Gallic acid	4	1	0.830?	Scheele,
	Boletic	45			Braconnot,
	Succinic		1.37	0.830?	Wenzel,
	Benzoic	2	1	0.792	Bucholz,
	Camphoric	1	0.5	0.792	Bucholz,
	Suberic	5.65	0.87	0.830	Brandes,
	C		In every		•
	Stearic 【	40	propor-	0.794	Chevreul,
	(		tion.		Í
- 1	Margaric		Do.		Chevreul,
- 1	C C	In every			
١	Oleic 【	propor-	Do.	0.816?	Ditto,
١	<i>(</i> .)	tion.			
	Elaiodic	Do.	Do.	0.792?	Bussy, Lecanu,
	Phocenic	Do.	Do.	0.794	Chevreul,
	Butyric	Do.	Do.	0.794	Ditto,
	Caproic	Do.	Do.	0.794	Ditto,
	Capric	Do.	Do.	0.794	Ditto,
	Ricinic	0.33		0.817	Bussy, Lecanu.

Mellitic acid dissolves readily in alcohol, and so do citric and tartaric acids, though these two are more soluble in water. Mucic acid, malic acid, and kinic acid, are insoluble in alcohol. Formic acid, and crystals of acetic acid, also readily dissolve. Meconic, pyromalic, pyrokinic, and pyrotartaric are also soluble in it.

Of Alkalies.

9. Alcohol dissolves potash and soda in great quantity. The stlution is at first colourless; but it becomes gradually yellowish

<sup>\*</sup> Taken from L. Gmelin's Handbuch der Theorischen Chemie, ii. 300-

brown, owing to a partial decomposition of the alcohol. Lithia is dissolved by it only in small quantity, and probably only when the alcohol is weak.

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Alcohol dissolves very little barytes, strontian, or lime, especially of the last. It does not render barytes or strontian water muddy; but it precipitates the lime from lime water. Yet, according to Bonaster, when alcohol is boiled upon lime, it takes up enough to restore the blue colour to litmus paper reddened by vinegar, and to be rendered muddy by oxalic acid. Magnesia is still less soluble in it; yet, according to Bonaster, if we boil alcohol on magnesia, it acquires the property of restoring the blue colour of litmus paper reddened by vinegar.

None of the earths proper are soluble in alcohol, nor any of the metallic oxides except those which have acid properties. Thus it dissolves chromic acid, and both arsenious and arsenic acids. Many of the metallic chlorides and iodides are soluble in it.

A great number of the salts are soluble in alcohol. But I of salts shall point out the solubility while treating of each salt in a subsequent part of this volume. I shall, however, exhibit the solubility of a few of these bodies in the following tables.

## 1. Substances dissolved in large quantities.

Names of the substances, Persulphate of iron			Tempera- ture.			240 parts of alcohol dissolve
Nitrate of cobalt+	_	_	54·5°	_		240 parts
copper+	•	•	54.5	•	•	240 parts
alumina+		•	54.5		•	240
lime‡ '	•	•		•	•	300
magnesia+	•		180.5	•	•	694
Muriate of zinc+		•	54.5			240
alumina+	•		<b>54·5</b>	•	•	240
magnesia+	•		180.5		•	1313
iron+	•	•	180.5		•	240
copper+	•	•	180.5		•	240
Acetate of lead copper*	•	•	154.5	•	•	240
Nitrate of zinc decomp	വർദ	44				
iron decom	ose	d†				
bismuth dec	eom]	posed	1+			

<sup>\*</sup> Withering, Phil. Trans. lxxii. 336.

#### 2. Suostances arssoivea in small quamules.

Names of the Substances.				240 parts of the Alcohol at the boiling tempera- ture dissolve
Muriate of lime+		•	•	240 parts
Nitrate of ammonia+	•	•		214
Corrosive sublimate	•	•	•	212
Succinic acid+	•	•	•	177
Acetate of soda+	•	•		112
Nitrate of silver+		<b>:</b>	٠.	100
Refined sugar+		•		<b>59</b>
Boracic acid+		•		48
Nitrate of soda+		•	•	23
Acetate of copper†		•	•	18
Muriate of ammonia+		•		17
Arseniate of potash+	•	•		9
Oxalate of potash+		•	•	7
Nitrate of potash+		•	•	5
Muriate of potash+		•	•	<b>5</b>
Arseniate of soda+		•	•	4
White oxide of arsenic	†	•	•	3
Tartrate of potash+		•	•	1
Nitrate of lead§				
Carbonate of ammonia	Q			

## 3. Substances insoluble in alcohol.

Sugar of milk	Sulphate of potash+
Borax+	soda+
Tartar+	magnesia+
Alum+	Sulphite of soda
Sulphate of ammonia+	Tartrate of soda and potash
lime	Nitrate of mercury+
barytes§	Muriate of lead+
iron	silver‡
copper†	Common salt+
silver+	Carbonate of potash
mercury	soda.
zine	

These experiments were made chiefly by Macquer and Wenzel.\* The alcohol employed by Macquer was of the specific

<sup>\*</sup> Verwandtschaft, p. 300. The solubility of all the salts marked† was ascertained by Wenzel; those marked ‡, by Macquer; and those marked §, by Withering.

gravity 0.840. Wenzel does not give the density of his alcohol; but as he compares it with that of Macquer, we may suppose it nearly of the same strength. As the solubility of salts depends upon the strength of the alcohol employed, the experiments of these chemists must be considered as defective, because they have confined themselves to one particular density. This defect is in part supplied by the following very valuable table of Mr. Kirwan's, constructed from his own experiments.\*

Solubility of Salts in 190 parts of Alcohol of different densities.

Salts.			Alcohol of		
Saits.	0.90 0	0.872	0.848	0.834	0.817
Sulphate of soda	0.	0.	0.	0.	0.
Sulphate of magnesia	1.	1.	0.	0.	0.
Nitrate of potash	2.76	1.		0.	0.
Nitrate of soda	10 •5	6.		0.38	0.
Muriate of potash	4.62	1.66		0.38	0.
Muriate of soda	5.8	3.67		0.5	
Muriate of ammonia	6.5	4.75		1 5	
Muriate of magnesia dried at 120°	21.25		23.75	36.25	50.
Muriate of barytes Ditto crystallized	1· 1·56		0·29 0·43	0·185 0·32	0·09 0·06
Acetate of lime	2.4		4.12	4.75	4.88

When alcohol containing certain saline bodies in solution is set on fire, its flame is often tinged of different colours according to the body. Thus nitrate of strontian and muriate of lime tinge it red; boracic acid and cupreous salts tinge it green; muriate of barytes gives it a yellow colour; nitre and corresive sublimate a yellow colour.

<sup>\*</sup> On Mineral Waters, p. 274.

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Alcoates explained. Mr. Graham has shown that several salts when dissolved in alcohol are capable of crystallizing in that liquid, and the crystals thus formed contain a quantity of alcohol essential to the crystalline form of the salt. Such salts he calls alcoates, to distinguish them from hydrated salts, the name given to those salts which contain water as essential to their crystalline form. The alcoates formed by Mr. Graham were all soft; and though most of them were crystallized, yet the shape of the crystals could not be made out. Mr. Graham prepared five alcoates, the composition of which was as follows:

Algoritad ablarida of aglaium

1. Alcoatea	l chlori	de of	calcru	m.
1 atom chloride of		_	•	7
$3\frac{1}{g}$ atoms alcohol	•	•	•	10.0625
				17.0625
2. Alcoated	nitrat	e of m	agnes	ria.
1 atom nitrate of m		-	•	9.25
9 atoms alcohol.	•	•	•	25.875
•				35.125
3. Alcoat	ed nitr	ate of	`lime.	
1 atom nitrate of	lime		•	10.25
$2\frac{1}{2}$ atoms alcohol	•	•	•	7.1875
				17.4375
4. Alcoated of	hloride	of m	angar	iese.
1 atom chloride of:	manga	nese	• ,	8
3 atoms alcohol	•	•	•	8.625
				16.625
5. Alcoate		ride oj	f zinc	
2 atoms chloride of	zinc	•	•	17.5
l atom alcohol .	•	•	•	2.875
				20.375*

When the crystalline shape of the alcoates comes to be more accurately studied than it has hitherto been, we may expect additional information respecting the part which water plays in saline combinations—a branch of chemistry hitherto very little examined.

## II. Pyro-acetic Spirii.

This liquid was discovered in 1807 by MM. Derosne History. during the distillation of verdigris, and the most remarkable of its properties determined.\* Proust, however, had previously obtained it by distilling acetate of lead and acetate of lime, and had pointed out some of its most remarkable properties.† And he shows that it had been known to Beccher, who considered it as alcohol, and that Baumé and Bernard Pluvinet had not entirely overlooked it. In 1809 it was again examined by Chenevix, who determined the proportion of it yielded by the different acetates, and subjected it to a more detailed examination than any preceding chemist.‡ In 1823 it was again examined by MM. Macaire and Marcet, who not only confirmed the results obtained by preceding experiments, but subjected it to analysis and determined its constitution.§

When the acetates are distilled in a retort by means of a Preparation, graduated heat always kept as low as possible, there comes over acetic acid dilitted with water, and pyroacetic spirit. The metallic base, mixed with charcoal, remains in the retort; and there flies off a mixture of carbonic acid and heavy inflammable gas. The metallic base is usually reduced to the metallic state, and the more difficult this reduction is, the greater is the quantity of pyroacetic spirit formed. The following table exhibits the result of the distillation of seven metalline acetates in a state of purity, as obtained by Mr. Chenevix:

<sup>\*</sup> Ann. de Chimie, lxiii. 267.

<sup>†</sup> Gehlen's Jour. iii. 37. Proust's paper was published in the Jour. de Phys. lvi. 200.

<sup>‡</sup> Ann. de Chim. lxix. 5.

<sup>§</sup> Bibliotheque Universelle, Oct. 1823. Annals of Philosophy (2d series), viii. 71.

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G pi	laseou oduci	ıs ts.	Liquid pro- ducts.			esidue retort.			
Total of gas.	Carb. hydrogen.	Carbonic acid.	Spirituous liquor.	Propor. of acid.	Sp. gravity.	Charcoal.	State of base.	Loss by the fire.	
20	12	<b>∞</b>	0	107:309	1.0656	0.020	Reduced.	0.36	Acetate of silver.
95	60	35	0.2	44.731	1.0398	0.14	Reduced.	0.61	Acetate of nickel
44	34	10	0.12	84.868	1.0556	0.055	Reduced.	19.0	Acetate of copper.
288	<b>8</b> 0	20	0.555	3.045	0.9407	<b>0.04</b>	Reduced.	0.37	Acetate of lead.
52	34	18	0.24	27.236	1.011	0.02	Black oxide.	0.49	Acetate of iron.
44	28	16	0.692	2.258	0.8452	0.05	White oxide.		Acetate of   Acetate of zinc.
52	32	20	0.94	1.285	0-8266	0.035	Black oxide.	0.555	Acetate of manganese.

The acetates of potash and of soda give a greater proportion of pyroacetic spirit than any of the metalline acetates. When acetate of barytes is distilled, the whole liquid product consists of this spirit without any mixture of acid whatever.

This pyroacetic spirit is quite the same in its properties from whatever acetate it is procured. No other genus of salts tried, as the oxalates, tartrates, citrates, yield this spirit. Acetic acid is not converted into it by heat. Mr. Chenevix distilled the same proportion of acetic acid five or six times through a red-hot porcelain tube; part of it was decomposed, the liquor became

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brown, and its specific gravity was diminished, but a considerable proportion remained unaltered. But if charcoal be put into the porcelain tube, the acid is destroyed by one distillation, and nothing obtained but water, carbonic acid, and heavy inflammable air.

Pyroacetic spirit is a white and limpid liquid. Its taste is Properties. at first acrid and hot, but it becomes cooling, and in some sort Its smell is peculiar, and is compared by Mr. Chenevix to that of a mixture of oil of peppermint and bitter almonds. Its specific gravity, when as pure as possible, is It burns with a flame, white exteriorly, but of a fine blue within, and leaves no residue. It boils at the temperature of 165°. It mixes with water, alcohol, and volatile oils, in any proportion. With hot olive oil it also mixes in any proportion: but with that oil cold it mixes only in certain proportions. dissolves a little sulphur and phosphorus, and is an excellent solvent of camphor. When hot it dissolves wax and tallow. A portion of these substances precipitates as the solution cools, but water still occasions a considerable precipitate in it. dissolves potash, and becomes darker coloured; but it may be obtained by distillation again unaltered. When mixed with sulphuric acid it blackens and is decomposed, and much charcoal is formed. When mixed with nitric acid it becomes yellow, and its properties are altered. Some oxalic acid is formed. Muriatic acid renders it brown. When distilled with this acid a combination takes place, and a substance is formed, possessing very different properties from muriatic ether.\*

When a current of chlorine is passed through this spirit a slightly yellowish colour is communicated. The resulting fluid has a strong smell. It speedily separates into two distinct fluids; the one thick, heavy, oily, and transparent, the other lighter and slightly opalescent. This last dissolves in water, and communicates to it a sweet taste.

Pyroacetic spirit being subjected to analysis by Macaire and Marcet, was found composed of

		-		
Carbon	•	•	•	<b>55·3</b>
Oxygen	•	•	•	36.5
Hydrogen		•	•	8.2
				100.0

Composition.

<sup>\*</sup> Chenevix; Ann. de Chim. lxix. 5.

## Chap. III. These numbers are proportional to

- 4 atoms carbon,
- 2 atoms oxygen,
- 31 atoms hydrogen.

Hence we may conclude that the constituents of pyroacetic acid are

2 atoms oxygen	•	•	2
4 atoms carbon	•	•	3
3 atoms hydrogen	a	•	0.375

5.375

or some multiple of these atomic ratios. The atomic weight is 5.375 or some multiple of that number. The difference between alcohol and pyroacetic spirit, if confidence can be put in the above analysis, is that alcohol contains twice as much hydrogen as pyroacetic spirit. This is rather an anomaly, considering that pyroacetic spirit is both more volatile and lighter than alcohol. It would be desirable on that account to repeat the analysis again with every possible care, in order to verify the results of MM. Macaire and Marcet.

## III. Pyroxylic Spirit.

History.

I do not know to whom we are indebted for the discovery of this liquid. In London and Glasgow it has been known for these 20 years, and I presume that it must have been discovered in Paris at least as early, as the manufactory of wood vinegar in that capital has existed for more than 20 years. I have been in the habit of employing it in lamps instead of alcohol for about 12 years. The first notice of it (so far as I know) in print was by M. Colin in the year 1819.\* He describes some of its most remarkable properties, and states his opinion that it is merely pyroacetic spirit containing an empyreumatic oil in solution. Dobereiner mentioned it in 1821, but mistook it for alcohol. MM. Macaire and Marcet made a set of experiments on it, and subjected it to analysis in 1828.† Since that time some of its properties have been investigated by M. L. Gmelin.†

When wood is distilled, the products are water, acetic acid,

<sup>\*</sup> Ann. de Chim. et de Phys. xii. 206.

<sup>+</sup> Bibliotheque Universelle, xxiv. 126. Annals of Philosophy (2d series), viii. 69.

<sup>•</sup> Handbuch der Theoret. Chimie, ii. 344.

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pyroxylic spirit, empyreumatic oil, and a black matter which is considered as analogous to pitch or rather tar. When the watery portion, freed as well as possible mechanically from the tar, is distilled at a low heat, the first portion that comes over is the pyroxylic spirit, which may be freed from acetic acid by agitation with lime or magnesia, and then distillation at a low temperature. But it is still contaminated to a great degree with empyreumatic oil, from which it has been hitherto impossible to purify it. It may be freed from a considerable portion of this oil by diluting it with water, which causes the greatest part of the oil to separate, disengaging the diluted spirit by decantation, and afterwards rectifying it by the same processes as succeeds with alcohol till it be again freed from the water; but this process is only partially successful, a considerable portion of oil still obstinately remaining. Gmelin says it may be nearly freed from oil by mixing it with its own weight of sulphuric acid and subjecting the mixture to distillation.

Pyroxylic spirit thus prepared is a transparent and colourless properties. liquid, having a strong pungent and somewhat ethereal smell, which Macaire and Marcet compares to that of ants, and Gmelin to that of acetic ether; but the smell of the pyroxylic spirit made in Glasgow (with which only I am acquainted) does not resemble either of these, but is quite peculiar. Its taste is strong, hot, pungent, and very disagreeable, derived obviously in part from the empyreumatic oil which it holds in solution.

Its specific gravity, in the most concentrated state in which I could procure it, was 0.8121. Macaire and Marcet found it to boil at 150°, and with this determination my experiments agree. Gmelin states its boiling point to be 137°, yet the specific gravity of the spirit which he examined was only 0.830. When completely freed from acetic acid it does not redden vegetable blues.

It burns with a very pale yellow flame inclining to blue, but the light is considerably greater than that given out by alcohol. It burns all away without leaving any residue, and the only products are carbonic acid and water.

It dissolves in alcohol in any proportion. With water it becomes opaque, obviously in consequence of the empyreumatic oil which it contains. It dissolves readily in oil of turpentine and in liquid potash, acquiring at the same time a yellowish colour. Camphor dissolves in it readily, but it does not dissolve oil. With sulphuric ether it unites likewise in all proportions. It dissolves a little sulphur and phosphorus, and is

Chap. III. a good solvent of common rosin and of shell lac. dissolved by it abundantly, and the solution has the same dark brown colour as the solution of iodine in alcohol.

> When the solution of this spirit in hydrated potash is distilled after an interval of a few days the pyroxylic spirit which comes over is quite free from empyreumatic oil. Here then is a method by which chemists may have it in their power to obtain this spirit in a state of purity.

> When mixed with nitric acid and distilled an ethereal liquid comes over, which, however, is quite different from nitric ether.

Sesquichlo. ride of carbo. hydrogen.

When  $\frac{1}{2}$  ounce measure of this spirit is mixed with 1 ounce measure of nitric acid and 2 ounce measures of muriatic acid in a flask, and a moderate heat applied, it soon begins to effervesce, and a gas comes over having an exceedingly pungent smell, and acting strongly on the nose and eyes. This gas burns with a bluish white flame. Its specific gravity I found 1.945, and on analyzing it was a mixture of three gaseous bodies in the following proportions in volume:

Deutoxide of a	azote	•	•	64.37
Azotic gas	•	•	•	<b>7·6</b> 8
A new gas	•		•	27.95

100.00

Water absorbs 5 times its volume of this gas, and oil of turpentine 34 times its volume.

The specific gravity of the new gas is 4.2361. 1½ times its volume of oxygen to burn it, and it forms its own volume of carbonic acid. When the combustion is made over mercury a quantity of calomel is formed at the same time. Hence it is a compound of

1 volume carbon vapour,

volume hydrogen gas,

11 volume chlorine gas,

condensed into one volume. It is a compound of

	OIIC V	OILLIII.		13 CL	COLLED	June Or
1	atom	carbon	•	•	•	0.75
1	atom	hydrog	en	•	•	0.125
11	atom	chlorine	•		•	6.75

7.625

and its atomic weight is 7.625. To this gas the name of socquichloride of carbohydrogen may be given.

According to Macaire and Marcet, when pyroxylic spirit is

mixed with thrice its weight of sulphuric acid and heated, a gas sect. III. is obtained which burns with a blue flame.

This spirit was subjected to analysis by Messrs. Macaire and Marcet, by volatilizing a given weight of it through red-hot black oxide of copper. The constituents deduced from this analysis were.

Carbon .	•	•	44.53
Hydrogen .	•		9.16
Oxygen .		•	46.31
This is equivalent to .			
4 atoms oxygen	•	•	4
5 atoms carbon		•	3.75
6 atoms hydrogen	•	•	0.75
			8.5

But no conclusion can be drawn from this analysis, because the spirit which they subjected to analysis was obviously contaminated with empyreumatic oil. I am very much inclined to suspect that it will be found to contain both less carbon and hydrogen compared with the oxygen than alcohol does.

#### SECTION III. -- OF SULPHURIC ETHER.

The term ether is applied by British and French writers Ether, what. indiscriminately to all the volatile liquids made by the action of acids on alcohol. But these liquids are divisible into two sets, exceedingly different from each other in their characters. One set is quite free from any portion of the acid employed in its preparation, and consists of the very same constituents as exist in alcohol, though the proportions are different; the other set consists of the acid employed in the formation of the ether, saturated with a peculiar volatile and combustible substance, which appears to be the same in all. Some of the latest chemical writers in Germany have confined the term ether to the first of these sets, and have distinguished the second set by the term naphtha. We have it not in our power to follow this example, as the word naphtha, in the English language, has been already appropriated to a very different substance. I shall satisfy myself, therefore, with separating the two kinds of ether from each other. I shall describe the first kind in this section, under the name of sulphuric ether, by which, or simply by the term ether, it is usually distinguished in this country; while in the next section I shall treat of the second kind of ethers under the name of acid ethers, though I must acknowledge that the name

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is not very appropriate. For these ethers when first formed have no acid qualities. They contain an acid indeed, but it is saturated with another substance which quite conceals its properties. But when these ethers are kept they gradually acquire acid qualities, whereas sulphuric ether may be kept for any length of time without undergoing much alteration in its nature.\*

History.

The method of making sulphuric ether is described in the dispensatory of Valerius Cordus, published at Nuremberg about the year 1540: from which Conrad Gesner transcribed it into his Thesaurus Euonymi de Remediis Secretis, published in 1552, where it is called Oleum Vitrioli dulce.† It appears to have been known, though not in a state of purity, both to Basil Valentine and Paracelsus. But in the writings of chemists published about the end of the 17th century, I have not been

- It appears from the observations of Planche and Gay-Lussac, that ether when kept for several years in a vessel not quite full, and often opened, generates some acetic acid. See Ann. de Chim. et de Phys. ii. 98 and 213. M. Henry has rendered it probable that this is owing to a small quantity of acetic ether which is usually mixed with sulphuric ether. Jour. de Pharmacie, xiii. 119.
- † Whoever will consider the formula given for preparing this Olcum Vitrioli dulce by Gesner, will be satisfied that it was very different from the dulcified acids of the moderns, and that it must have been a mixture of alcohol, ether, and sweet oil of wine. The following is the passage of Gesner, as quoted by Hoffman, from whom has been taken the historical facts respecting the knowledge of ether possessed by the alchymistical writers.-"Recipe vini ardentis acerrimi et ter sublimati uncias quinque, olei vitrioli austeri tantundem, misce in venetiano vitro, et pone in cucurbitam parvam angusto orificio, et luto optimo orificium claude, dimitte ita per integrum mensem aut duos. Deinde effunde in cucurbitam, cui sit immediate annexum alembicum, cujus figuram subjiciemus, pone deinde in parvam fornacem, ac dimidiam ejus partem cinere obrue, postea applica recipientem et luto juncturam claude diligenter, et extrahe uncias sex vini ardentis quas infudisti. Ut vero tutius hoc fiat, pone in balneum Mariæ; sic solum vinum absque oleo ascendet. Cum extraxeris autem per balneum infusas uncias sex vini usti. pone id, quod residuum est, in fornacem, ut arena mediam cucurbitæ partem attingat, ac novo et vacuo recipiente coque non magno applicato, luto juncturam diligenter claude. Accende deinele modestum ignem, et sensim extrahe omnem humiditatem quæ relicta est in cucurbita, donec nihil humidi amplius in fundo appareat; adhibita semper maxima cura et diligentia, ut ignem ita modereris, ne ebulliat usque ad alembici canalem. Nam si hunc ebullitio attigerit, sedare non potes, neque prohibere, quin in receptaculum egrediatur, ac totum oleum perdat; solet enim facilime ebullire. Tum videbis duo comineri in eo, aqueum videlicet humorem ac pinguem; segregabis vero unum ab altero statim, ita ut mbil aqueum in oleo relinquatur, nam aqua illa oleum corrumpit; segregatum oleum usui reserva."

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able to find any traces of it,\* except in those of Mr. Boyle. He was evidently acquainted with it, as appears from different passages of his writings,† though he no where describes it particularly. But it was a paper in the Philosophical Transactions for 1730, by a German who called himself Dr. Frobenius, describing several of its most singular properties, that first drew the attention of chemists to this curious liquor.‡ In this paper it first received the name of ether. The German chemists long distinguished it by the name of naphtha.

1. Sulphuric ether is usually prepared by the following propreparation. cess: A mixture of equal parts of alcohol and sulphuric acid is put into the retort, to which a large receiver is then luted. It is proper to surround the receiver with ice, or at least with cold water. Heat is applied; and as soon as the mixture boils, the ether comes over and is condensed, and runs in large strike down the sides of the receiver. As soon as it amounts to one half of the alcohol employed, the process must be stopped. The ether, thus obtained, is not quite pure. It always contains alcohol, and is never free from sulphurous acid.

The separation of the liquid from the sulphurous acid, with which it is mixed, is called the rectification of the ether. The usual method, and I may add, the best, is the following, first employed by Mr. Wolfe: Fill three-fourths of a bottle with the impure ether, add a little water and a portion of slacked lime. Agitate the bottle with violence, and keep it for some time in water before taking out the cork. If the smell of the acid be not removed, add a little more lime, and agitate a second time. Decant off the ether into a retort, and distil it over.

The first portion of liquid that comes over during the distillation is merely alcohol impregnated with a little ether. Common ether is in reality a mixture of ether and alcohol. The usual method of separating this liquid is by mixing the ether with water, and then proceeding to distillation with a very

<sup>\*</sup> The Olcum Vitrioli dulce of Lemery, for instance, is very different from that described by Gesner. (See his Cours de Chymie, p. 502.)

<sup>+</sup> See Shaw's Boyle, i. 530; and i. 269; where the process for making ether, and some of its most remarkable properties, are detailed at length.

<sup>†</sup> Phil. Trans. xxxvi. 283. This paper is little else than a rhapsody in the alchymistical style. At the end of it there is a note by Mr. Godfrey, (Hankwitz,) Mr. Boyle's operator, mentioning the experiments formerly made upon it by Mr. Boyle and Sir Isaac Newton.

<sup>§</sup> Frobenius' process was first published in the Philosophical Transactions, vol. xli.

<sup>||</sup> Proust, Ann. de Chim. xlii. 256.

Chap III. moderate heat. But Mr. Lowitz has shown that this method does not succeed. The following process yielded him an ether much purer than any that had been previously obtained: Into 16 parts of ether, of the specific gravity 0.775 in the temperature of 60°, he threw dry powdered salt of tartar, till the last portions were no longer wetted by the liquor. The mixture being allowed to digest, the ether was then drawn off. specific gravity was now only .746. By this means it was deprived of the water which it contained. To remove the alcohol, dry powdered chloride of calcium was thrown into the liquid in the same manner, as long as it would dissolve. standing, the mixture separated into two portions; the alcohol holding the salt in the solution sunk to the bottom; the ether swam on the surface. When separated from the inferior liquor, its specific gravity was now only .632 in the temperature of 60°. It was, therefore much purer than any former ether described by chemists, since it never before had been procured lighter than 0.725.\* The ether thus prepared contains a little of the salt, from which it may be freed by distillation. But in that case its specific gravity increases. The reason seems to be, that the purest portion of the ether assumes the form of elastic M. Theodore de Saussure purified ether by nearly the same process, excepting that he distilled it off the muriate of He obtained it of the specific gravity 0.7155 at the temperature of 68°†. By the same process Lowitz could not obtain ether of a lower specific gravity than 0.716. Gay-Lussac removed the alcohol by agitating the ether with twice its weight of water. The washed ether was left in contact with quicklime for 12 days and then distilled gradatim. specific gravity was 0.7119, at the temperature of 77°. Richter obtained it of a specific gravity as low as 0.706 at 60°. specific gravity of the purest ether, which Boullay was able to makc, was 0.690.

> Boullay has shown that we may form this ether, though we substitute phosphoric acidt or arsenics acid for the sulphuric. And Desfosses has found that the same process succeeds when we employ fluoboric acid.

Properties.

Ether, thus obtained, is a limpid and colourless liquor, of a very fragrant smell, and a hot pungent taste.

It is so volatile that it can scarcely be poured from one vessel

<sup>\*</sup> Lowitz, Crell's Annals, 1796, i. 429. † Annals of Philosophy, iv. 40. § Ibid. lxxviii. 284. 'I Ann. de Chim. lxii. 192.

Ann. de Chim. et de Phys. xvi. 72.

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to another without losing a considerable portion of it by evaporation. When poured out in the open air, it disappears in an instant; and, during its evaporation, produces a very considerable degree of cold. If a glass vessel containing water, and surrounded with a cloth, be dipped into ether, two or three times, and the ether each time be allowed to evaporate from the cloth, the water in the glass freezes. In the open air ether boils at 96°, and in a vacuum at - 20°. Were it not, therefore, for the pressure of the atmosphere, it would always exist in the gaseous state. But Dr. Bestock has noticed that it may be heated in a clean glass tube as high as 150° or even higher before it emits bubbles. If when it is at that temperature we throw into it any solid body, as metal filings, or chips of wood, or fragments of glass, it immediately boils with great violence, and the bubbles of vapour all issue from the surface of the body introduced. Though the temperature of the ether was lowered the boiling still continued till the heat sank to 102°, and in one case to 96°, which is the true boiling point of ether.\*

When exposed to the open air it speedily assumes the gaseous form. This happens, for instance, if a little of it be poured into a glass phial. The vapour of ether displaces a considerable portion of the air of the phial, and is not soon dissipated. Ingenhousz has shown that the specific gravity of this vapour is very considerable.†

Mr. Dalton found it 3·125, the specific gravity of common air being 1.‡ Gay-Lussac has determined the specific gravity of this vapour with much care. According to his experiments, it is 2·5860, that of air being 1.§ The determination of Gay-Lussac has been confirmed by M. Despretz, who found the specific gravity of ether vapour 2·5808.

According to Fourcroy and Vauquelin, it freezes or crystallizes when cooled down to — 46°.¶ But Thenard assures us that it remains liquid though exposed to a cold of — 58°. Hence the remarks of Fourcroy and Vauquelin can apply only to the common ether of the shops.

<sup>\*</sup> Annals of Philosophy (2d series), viii. 196. The same phenomenon appears when alcohol, or even water, is heated in glass tubes, as has been observed by Dr. Bostock. This curious subject has been investigated by M. Gay-Lussac; but no satisfactory explanation of it has been hitherto given.

<sup>+</sup> See his Nouvelles Experiences, p. 180.

<sup>#</sup> Manchester Memoirs, iii. 260. Second Series.

<sup>§</sup> Ann. de Chim. et Phys. i. 218. | Ann. de Chim. et de Phys. xxi. 746.

<sup>¶</sup> Ann. de Chim. xxix. 289.

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Neither oxygen gas nor common air produce any effect upon ether in moderate temperatures; but in high temperatures the case is very different. Ether is exceedingly inflammable, and when kindled in the state of vapour burns with rapidity, with a fine white flame, and leaves behind it a trace of charcoal. During its combustion carbonic acid is generated. How well soever it has been rectified, it always exhibits traces of sulphuric acid.\*

When ether is admitted to any gaseous body standing over mercury, it doubles the bulk of the gas, as Dr. Priestley first observed. If oxygen gas, thus expanded by ether, be presented to a lighted candle, the ether burns with great rapidity, but produces no explosion. But if one part in bulk of this expanded oxygen be mixed with three parts of pure oxygen gas, and kindled, a very loud explosion takes place: the products are water and  $2_{\overline{z}}$  parts of carbonic acid.† Mr. Cruickshanks, to whom we are indebted for this instructive experiment, found, that one part of the vapour of ether takes 6.8 parts of oxygen gas to consume it completely; and from the relative proportions of the two products, he concluded that the carbon which ether contains is to its hydrogen as five to one.

According to Dalton, one volume of ether requires for its combustion six volumes of oxygen; the residue consists of four volumes of carbonic acid.‡

Composition.

Now it is obvious that four volumes of the oxygen gas must have gone to the formation of carbonic acid gas; the remaining two volumes of oxygen must have gone to the formation of water, and they must have united with a quantity of hydrogen, which, had it been in the gaseous state, would have amounted to 4 volumes. Carbonic acid gas contains its own volume of carbon in the gaseous state. It follows, therefore, from the preceding facts that 1 volume of vapour of ether contains

4 volumes carbon,
4 volumes hydrogen,
5 condensed into 1 volume.

I have shown in a preceding part of this work, that a volume of carbon vapour and a volume of hydrogen gas are proportional to an atom of each. Hence that portion of ether which is combustible, is a compound of

4 atoms carbon,

4 atoms hydrogen.

<sup>•</sup> Scheele, ii. 108. † Cruickshanks, Nicholson's Journal, v. 205. † Manchester Memoirs, iii. 179. Second Series.

The vapour in its gaseous state is then a compound of 4 volumes (or atoms) of carbon vapour, and 4 volumes (or atoms) of hydrogen gas condensed into one volume. We obtain the specific gravity, therefore, by adding together 4 times the specific gravity of these two bodies.

 $= 0.4166 \times 4 = 1.6666$ Carbon Hydrogen =  $0.0694 \times 4 = 0.2777$ 

### 1.9444

But the specific gravity of ether vapour was found to be 2.5808. If from this we subtract 1.4444, there will be a remainder cf 0.6364, which comes very near 0.625, = specific gravity of vapour of water. It is evident from this that a volume of ether vapour, beside the gaseous compound of 4 volumes carbon vapour, and 4 volumes hydrogen gas, contains also a volume of the vapour of water.

Though the combustible portion of ether be analogous in its Gaseous combinations of composition to olefiant gas, and though if two volumes of olefiant carbon and hydrogen, gas were condensed into one, they would constitute a volume of the combustible portion of ether, yet it is obvious that it constitutes a quite different compound from olefiant gas, and constitutes one of the numerous tribe of substances, composed of an equal number of atoms of carbon and hydrogen, and distinguished from each other by the number of atoms of each in an integrant particle or volume of the respective body. of these bodies have been already described in this work, namely:

- 1. Carbo-hydrogen, obtained when pyroxylic spirit is treated with aqua regia. It is a gas, a volume of which contains 1 volume (or atom) of carbon vapour and 1 volume (or atom) of hydrogen condensed into 1 volume. Hence its specific gravity is 0.4861, and for complete combustion it requires 1 times its volume of oxygen gas and forms its own volume of carbonic acid gas.
- 2. Olefiant gas obtained by heating a mixture of four parts by weight of sulphuric acid with 1 part of alcohol. It consists of 2 volumes (or atoms) of carbon vapour and 2 volumes (or atoms) of hydrogen gas, united together and condensed into one volume. Hence its specific gravity is 0.9722. It requires thrice its volume of oxygen to burn it, and it leaves twice its volume of carbonic acid behind.
- 3. The vapour of oil gas which may be called trito-carbohydrogen, as it consists of three volumes (or atoms) of carbon

Chap. III. vapour and three volumes (or atoms) of hydrogen gas united together, and condensed into one volume. Hence its specific gravity is 1.4583. It requires 4.5 times its volume of oxygen gas to burn it, and it leaves behind three times its volume of carbonic acid gas.

4. The combustible part of ether vapour which may be called tetarto-carbo-hydrogen, as it is a compound of 4 volumes (or atoms) of carbon vapour and 4 volumes (or atoms) of hydrogen gas condensed into one volume. Hence its specific gravity It requires 6 times its volume of oxygen gas to burn At, and it leaves behind it 4 times its volume of carbonic acid gas.

Theodore de Saussure analyzed ether also by burning it with oxygen gas. He determined the quantity of carbonic acid formed, and of oxygen gas consumed. This gave him the carbon and hydrogen in the combustible portion of the vapour; what was wanting to complete the weight of the vapour consumed he considered as water. The constituents found in this way were

			100.00*
Oxygen .	•	•	17.62
Carbon .	•	•	67.98
Hydrogen	•	•	14.40

Now these numbers are nearly equivalent to

5 atoms hydrogen, 3.93 atoms carbon, 0.8 atom oxygen.

This comes as nearly as can be expected to

5 atoms hydrogen, 4 atoms carbon, 1 atom oxygen,

which are the atomic proportions resulting from Mr. Dalton's analysis. The experiments of Saussure, therefore, serve as an additional confirmation of the constitution of ether as above deduced. It is therefore a compound of

1 volume tetarto-carbo-byo	drogen	•	1.9444
1 volume vapour of water	•	•	0.6250

2.5694

Hence the true specific gravity of ether vapour must be 2.5694, and its atomic weight is evidently 4.625.

<sup>\*</sup> Annals of Philosophy, iv. 40.

The analysis of Dalton and Saussure have been confirmed by Dumas and Boullay, who obtained

 Carbon
 .
 .
 65.05

 Hydrogen
 .
 .
 13.85

 Oxygen
 .
 .
 21.24

100.14\*

equivalent to

4.08 atoms carbon, 5.2 atoms hydrogen, 1 atom oxygen,

numbers approaching theory still nearer than Saussure's.

It resembles alcohol in being a compound of 1 volume of a combustible carbo-hydrogen and 1 volume of vapour of water condensed into 1 volume. But the carbo-hydrogen is different in each; in alcohol it is olefiant gas, in ether it is tetarto-carbo-hydrogen. Hence the reason of the greater specific gravity of ether vapour and of its superior combustibility. Doubtless it is the aqueous vapour in both that prevents the combustibility from being so great and the light emitted so splendent as when olefiant gas itself is burnt.

Ingenhousz was the first who ascertained that the vapour of ether detonates with common air and oxygen gas. His account of the experiment was first published in a letter to Dr. Priestley, in one of the original volumes of that philosopher on air, and likewise in the 69th volume of the Philosophical Transactions. His method was exceedingly simple. A single drop of ether let fall into a bottle holding about 10 cubic inches of air, gives it the property of detonating. Too much ether destroys the detonation. With oxygen gas the same method succeeds.

When ether, in the state of vapour, is made to pass through a red-hot porcelain tube, it is decomposed completely, and a great quantity of carburetted hydrogen gas is obtained.‡ Saussure, junior, repeated the experiment with precision. He passed 1103 parts of the ether through a red-hot porcelain tube; the products were as follows:  $5\frac{1}{4}$  parts of charcoal in the tube, 3 parts of volatile oil crystallized in thin scales and smelling of benzoin; 43 parts of a volatile oil nearly black, partly fluid and partly of the consistence of honey; 3 parts of water, and 948 parts of heavy inflammable air. The loss, amounting to

<sup>\*</sup> Ann. de Chim. et de Phys. xxxvi. 299.

<sup>†</sup> See Ingenhousz' Experiences, p. 171.

<sup>†</sup> Dutch Chemists, Jour. de Phys. xlv. 184.

Chap III. 100.75 parts, was chiefly owing to the escape of oil in the state of vapour.\*

> If we fill a bottle capable of holding three or four English pints with chlorine gas, formed by the action of muriatic acid on chlorate of potash, taking care to expel the water as completely as possible, and then throw into it about a drachm, or half a drachm, of good ether, covering its mouth immediately with a piece of light wood or paper, in a few seconds white vapour will be perceived moving circular in the bottle; this will be soon followed by an explosion accompanied with flame; at the same time a very considerable quantity of charcoal will be deposited, and the bottle will be found to contain carbonic acid gas.+

> I shall now state the action of ether on the principal chemical substances with which it is likely to be brought in contact.

Combines with water

If we mix together equal volumes of ether and water in a stoppered phial, and after agitation set down the phial, the liquid speedily separates into two layers. The uppermost is the ether, not quite free from water, and the undermost the water holding in solution about  $\frac{1}{10}$ th of its weight of ether, as was first ascertained by Count Lauraguais. † The specific gravity of the water so impregnated is 0.96, and it begins to boil (according to Dalton) at 203°, disengaging at first pure ether.

and alcohol.

In alcohol it dissolves in all proportions. Common ether always contains alcohol, from which it is easily freed by agitation in water, as has been already explained in a former part of this section. The following table, drawn up by Mr. Dalton. shows the specific gravity of various mixtures of ether and alcohol.

Ether.	Alcohol	١.		Sp. gr.	Ether, Alcohol,			Sp. gr.
100 +	0		•	0.720	40 + 60			0.792
90 +	10	•	•	0.732	30 + 70			0.804
80 +	20	•	•	0.744	20 + 80	•		0.816
70 <b>+</b>	30	•	•	0.756	10 + 90			0.828
60 +	40			0.768	0 + 100		٠	0.830
50 <b>+</b>	<b>50</b>			0.780 ~				

If we agitate small pieces of phosphorus at the temperature of 60° in ether free from alcohol, we obtain a transparent

- \* Nicholson's Journal, xxi 323.

A solution of 1 part ether in 2 or 3 parts of alcohol constitutes Hoffmarti's liquor anodynus mineralis, or Hoffmann's white drops, so commonly employed in Germany in nervous affections.

colourless solution, containing  $\frac{1}{80}$ th of its weight of phosphorus. But ether, if it contains alcohol, dissolves only  $\frac{1}{240}$ th of its weight of phosphorus. The solution smells of phosphorus, and burns when dropped into boiling water. When mixed with alcohol it becomes milky, owing to the precipitation of the phosphorus.\*

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Ether was supposed incapable of acting on sulphur, except sulphur, when both vere in the state of vapour, according to the experiments of Lauraguais; but Favre has shown that a solution may be obtained by digesting flowers of sulphur in cold ether, and that the solvent power of the ether is promoted by exposure to the light. By a month's digestion he dissolved nearly one part of sulphur in 12 of sulphuric ether; the solution was nearly colourless, but had the taste and smell of sulphuretted hydrogen.

Ether dissolves iodine, and the solution has a brown colour. iodine,

It dissolves also the chlorides of carbon.

It absorbs 2.17 times its volume of carbonic acid gas, 5 times its volume of cyanogen gas, 0.15 volume of azotic gas. Ammoniacal gas, and hydrocyanic acid vapour, are also absorbed by it in considerable quantity. It absorbs muriatic acid gas, and dissolves in liquid muriatic acid without the formation of muriatic ether. Fluosilicic acid gas is absorbed by it abundantly.

Ether dissolves about 4 per cent. of its weight of hydrated potash, potash. The solution is yellowish, and rather heavier than ether.

It dissolves several of the metallic sulphurets, chlorides, bro- and other bodies, and iodides; but always to a less extent than alcohol does. In general these solutions undergo speedy decomposition, acids being generated.

It is an excellent solvent of chromic acid.

It dissolves \( \frac{1}{4} \)th of its weight of nitrate of uranium: both the chlorides of iron are taken up by it. The solution of the sesquichloride is dark yellow and very acid. When we agitate ether with an aqueous solution of these chlorides, and leave the liquid at rest, the ether separates and carries with it all the iron chlorides. It has been long known that ether separates in the same way the chloride of gold from its aqueous solution. It dissolves a little of the chloride of cobalt, and acquires a sky blue colour. Both chlorides of copper are dissolved by it in small quantity.

It dissolves from 1th to 1th of its weight of corrosive

\* Brugnatelli; Ann. de Chim. xxiv. 73.

† Gehlen's Jour. iv. 227. ‡ Boullay.

II.

sublimate, and when agitated with the aqueous solution of corrosive sublimate it abstracts it from the water. According to Vogel, when this solution is exposed to the light it deposites calomel, but with Dr. J. Davy this deposition did not take place. He found the specific gravity of ether saturated with corrosive sublimate to be 1.08. It is a good solvent of chloride of platinum.

Acids dis. solved by it, It dissolves Oxalic acid; in small quantity.

Formic acid.

Acetic acid; separated by water.

Meconic acid.

Gallic acid.

Benzoic acid;  $\frac{1}{2.5}$ th of its weight.

Camphoric acid;  $\frac{1}{3}$  at 47°.

Suberic acid;  $\frac{1}{10}$  at 39°,  $\frac{1}{8}$  at 50°,  $\frac{1}{6}$  at 95°. Brandes.

Cholesteric acid.

Ambreic acid.

Stearic; 0.12 part.

Margaric.

Oleic; I part in 29.1 of boiling ether.

Elaiodic.

Phocenic.

Butyric.

Caproic.

Capric.

Hircic.

Cevadic.

Ricinic; in 1 ether at 64°.

The pyroacids.

Finally, sulphuric ether combines readily with all the other ethers; it dissolves also pyroacetic and pyroxylic spirits, volatile oils, fats, many resins, and not a few both vegetable and animal bodies which it would be needless to enumerate here. It dissolves also several fixed oils and several bitumens.

Theory of etherification.

It will be proper now to make a few remarks respecting the theory of etherification, which has engaged a good deal of the attention of chemists. To understand the subject we must attend to what takes place when sulphuric acid and alcohol are mixed, and the products successively evolved. Upon this branch of the subject much light has been thrown by the experiments of Mr. Hennell.\*

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When equal weights of alcohol and sulphuric acid are mixed together without the application of any heat, about one-half of the sulphuric acid is converted into sulphovinic, which (as has been explained in a preceding part of this volume) is a compound of

2 atoms sulphuric acid, 1 atom tetarto-carbo-hydrogen.

When this mixture is distilled ether is formed, and passes over into the receiver, while the sulphovinic acid disappears. It would appear from this that the ether originates from the tetarto-carbo-hydrogen in the sulphovinic acid. This substance, in order to be converted into ether, requires only to quit the sulphuric acid with which it was previously combined, and to unite with an atom of water in its stead. The action of heat seems to produce this effect in consequence of the great difference between the volatility of sulphuric acid and aqueous vapour. The sulphuric acid thus set at liberty acts upon a new portion of the alcohol, doubtless converting it into sulphovinic acid, which the heat afterwards decomposes. That this view of the subject is correct, seems proved by the direct experiments of Mr. Hennell, who mixed a portion of sulphovinate of potash with the quantity of sulphuric acid requisite to saturate the potash, and distilling the mixture, a quantity of ether was obtained.

In preparing ether the ebullition is continued till white vapours make their appearance, and the smell of sulphurous acid is perceived. The receiver must then be changed, for no more ether will be formed unless more alcohol be added to the acid mixture. If we still continue the heat after changing the receiver, sulphurous acid is produced abundantly, and a yellowish liquid comes over quite different from ether. it with a sufficient quantity of liquid potash, to saturate the sulphurous acid which it contains, and then apply heat enough to drive off the little ether which it may contain, what is called the sweet oil of wine will remain floating on the surface of the watery liquid. This liquid may be obtained in greater abundance by distilling a mixture of equal volumes of alcohol and sulphuric acid, and purifying the product by agitating it with a weak solution of carbonate of potash. Thus obtained it has a yeliow colour, a fragrant smell, a bitterish and pungent taste, and a specific gravity of 1.060. It does not mix with ether, but combines with alcohol, and it produces no change on vege-table blues. Mr. Hennell has shown by satisfactory experiments that oil of wine is a compound of

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2 atoms sulphuric acid,

2 atoms tetarto-carbo-hydrogen.

When it is kept, one-half of the tetarto-carbo-hydrogen separates from it in a crystalline form, and the oil of wine becomes sulphovinic acid. We see from this how different tetarto-carbo-hydrogen is from olefiant gas; the former being a solid and the latter a gaseous body.

If we agitate oil of wine with a sufficient quantity of water, it is converted into sulphovinic acid, and the excess of tetarto-carbo-hydrogen is separated in the form of a bright amber colured oil, of the consistency of castor oil. Its specific gravity is 0.9. It is insoluble in water, very soluble in ether, and somewhat less so in alcohol. It burns with a brilliant flame, throwing off some carbon. When analyzed by red-hot oxide of copper, it gave very nearly equal atoms of carbon and hydrogen.

These facts, for which we are chiefly indebted to Mr. Hennell, will enable us to appreciate the accuracy of the theory of etherification, first broached by Fourcroy and Vauquelin, and still pretty generally adopted by chemists.

These chemists were of opinion that the only difference between alcohol and ether is that the former contains twice as much water as the latter. Sulphuric acid acts simply by abstracting one-half of the water of the alcohol; the spirit thus modified flies off under the form of ether. This theory possesses the merit of extreme simplicity, and when it was advanced it appeared unobjectionable. It has been lately supported by an elaborate set of experiments by Dumas and Boullay.\* But I consider it to be unnecessary to enter upon any discussion, because their reasoning is utterly at variance with the whole phenomena of the formation of ether.

It is certainly true that ether contains only half the water that exists in alcohol; but it is no less so that the other constituent of ether is not the same with the combustible constituent of alcohol. Alcohol is a compound of

l atom water,

1 atom olefiant gas.

Ether of

l atom water,

1 atom tetarto-carbo-hydrogen.

Olefiant gas is an elastic fluid, tetarto-carbo-hydrogen a liquid or solid body; olefiant gas is a compound of

<sup>\*</sup> Ann. de Chim. et de Phys. xxxvi. 294.

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§ 2 atoms carbon, 2 atoms hydrogen.

While tetarto-carbo-hydrogen is a compound of

{ 4 atoms carbon, 4 atoms hydrogen.

The effect produced by the sulphuric acid on the alcohol is to separate the olefiant gas from the water with which it was before in combination. And it is not unlikely that the strong affinity of sulphuric acid for water may contribute to this effect. One portion of the sulphuric acid may combine with the olefiant gas, and another with the water. But the olefiant gas when thus united to the acid undergoes a farther modification: two atoms of it are combined together to constitute one atom of tetarto-carbo-hydrogen. How this new combination takes place cannot at present be explained, as we have no exact notions upon what the many different modifications of carbo-hydrogen at present known depend. But it appears from the experiments of Mr. Hennell that we can extract either ether or alcohol at pleasure from sulphovinic acid. When dry sulphovinate of potash was mixed with the quantity of sulphuric acid necessary to saturate the potash, ether was obtained; but when the salt, previously dissolved in water, was mixed with the same quantity of sulphuric acid, and distilled, alcohol was obtained. In the former case the combination consisted of an atom of water and an atom of tetarto-carbo-hydrogen, in the latter of an atom of water and an atom of olefiant gas. It appears from this that water and heat have a tendency to convert tetartocarbo-hydrogen to olefiant gas.

We cannot easily explain the cause of the oil of wine being formed when the alcohol is greatly diminished. The charry matter formed seems to act upon the sulphuric acid. It probably contains a quantity of tetarto-carbo-hydrogen, which unites with the sulphovinic acid, and converts it into oil of wine.

#### SECTION IV. --- OF ACID ETHERS.

The ethers, which I distinguish by the appellation acid, not because they possess acid properties, but because they contain an acid as one of their constituents, are twelve in number, and naturally divide themselves into two sets, namely: those that contain a hydracid or chlorine as a constituent, and those which contain an oxygen acid. The first set comprehends 4 ethers, namely: muriatic ether, chloric ether, hydrobromic ether, and hydriodic ether. The second set consists of 8 ethers, namely:

Chap. III. nitric ether, oxalic ether, acetic ether, benzoic ether, formic ether, tartaric ether, citric ether, and malic ether.

All these ethers are made by distilling mixtures of alcohol, and the acid which enters into each as a constituent. times it is requisite to add a certain portion of sulphuric acid to the mixture. They are, each, named by adding the term ether to the acid employed in its formation, and which exists in it as a constituent.

#### 1. Muriatic Ether.

History.

After the discovery of sulphuric and nitric ether, various attempts were made to obtain ether by the action of muriatic acid on alcohol: but this acid in its usual state is too much diluted with water to act with much energy upon alcohol. was thought necessary, therefore, in order to procure muriatic ether, to employ the acid in a different state. The method of obtaining this ether is as follows:

Pure alcohol is saturated with muriatic acid gas as free from water as possible. The following is the formula recommended by Mr. Basse. Keep a quantity of common salt for an hour in a state of fusion, in order to deprive it of its water of crystallization. Put 20 parts of this salt into a tubulated retort, to the beak of which is fitted a bent tube, plunging into a Woolfe's bottle, containing 10 parts of alcohol as strong as possible.

Introduce into the retort, in small quantities at a time, 10 parts of the most concentrated sulphuric acid, allowing the common air to escape from the bottle containing the alcohol; then distil in a sand bath till the muriatic acid comes over, keeping the alcohol bottle as cool as possible during the process. The alcohol, thus saturated with acid, is put into a retort, and one-half of it distilled over. Agitate this portion with an alkaline ley, and then decant off the ether which swims on the surface: it usually amounts to  $2\frac{1}{q}$  parts.\*

Very little was known of the properties of muriatic ether, till Gehlen published a dissertation on the subject in 1804.+ He employed two processes: 1. the action of the fuming liquor of Libavius on alcohol; 2. the process of Basse detailed above. Both of them furnished ether, the peculiar properties of which he has described with accuracy. Thenard published three dissertations on it in 1807, pointed out the simplest process for

<sup>\*</sup> Jour. de Chim. iv. 86.

<sup>+</sup> Gehlen's Jour. ii. 206.

<sup>‡</sup> Mcm. d'Arcueil, i. 115, 140, 337.

obtaining it, examined the effect of chlorides on alcohol, described the properties of muriatic ether in detail, and made a set of experiments to ascertain its constituents. To the dissertations of these two chemists we are indebted for all that we know of this very remarkable substance.

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The process recommended by Thenard for procuring this Formation. ether is the following: Equal bulks of muriatic acid and alcohol, both as strong as possible, are put into a retort, of such a size as not much more than to hold the mixture. A few grains of sand should be put into the retort, to prevent the violent boiling which might otherwise take place. From the beak of the retort a tube passes into a glass jar, twice the size of the retort, and furnished with three mouths. This jar should be half filled with water, of the temperature of about 70°. Into the second mouth a straight tube of safety is luted, and into the third a tube, which passes into a water trough to receive the gas. When heat is applied, the mixture soon emits bubbles. There passes into the receiver alcohol with acid and water: but the whole of the ether makes its escape in the state of gas, and must be received in proper vessels. From 500 grammes of acid and the same bulk of alcohol, between 20 and 30 litres of ethereal gas are obtained. Or, in round numbers, a mixture of acid and alcohol, weighing about 30 ounces troy, will yield between 1220 and 1830 cubic inches of ethereal gas.

This gas is colourless, it has a strong ethereal smell, and a Properties. sweetish taste. It produces no change on the infusion of litmus, the syrup of violets, or lime water. Its specific gravity is 2.219, that of air being 1. At the temperature of 64° water dissolves its own bulk of this gas.

When exposed to a cold of 52°, it loses its aërial form and becomes liquid ether. It may be procured abundantly in that state by passing it into a dry glass jar surrounded with ice. Muriatic ether, in its liquid state, is colourless like water, very liquid, has no action on vegetable blues, and has the same smell and taste as in the gaseous state. At the temperature of 41°, Thenard found it of the specific gravity 0.874.\* It is much more volatile than alcohol, or even sulphuric ether, assuming the gaseous state when not hotter than 64°. None of the usual tests indicate the presence of any muriatic acid. It does not affect vegetable blues, nor give out acid when agitated with an

<sup>\*</sup> Basse obtained it of the specific gravity 0'820, and Gehlen of 0.445. Here we must consider weight as a mark of purity. Hence it is obvious that the muriatic ether of the German chemists was less pure than Thenard's.

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alkaline ley, or occasion an immediate precipitate when mixed with nitrate of silver. But when brought in contact with a combustible it burns readily with a green coloured flame, and a very considerable portion of muriatic acid is immediately disengaged in the state of vapour. This fact then so singular was first observed by Gehlen: it has been minutely examined by Thenard. When allowed to remain for a long time in contact with an alkali, it does give out a portion of muriatic acid, and it slowly produces a precipitate in nitrate of silver after the interval of several days, and the quantity of precipitate increases with the time. But in neither case is the ether decomposed, or deprived of the property of giving out muriatic acid when burnt.

Thenard has endeavoured to ascertain the composition of muriatic ether. From the quantity of muriatic acid which disappears during its formation, he has calculated that 100 parts of muriatic ether contain 29.44 of acid. By mixing determinate portions of muriatic ether gas with oxygen gas, firing the mixture, and ascertaining the products, which are only carbonic acid and water, he endeavoured to ascertain the proportion of the other constituents. The following is the result of his examination:

Composition.

29.44 muriatic acid 36.61 carbon 23.31 oxygen 10.64 hydrogen

#### 100.00\*

It is generally admitted that it is a compound of one atom of tetarto-carbo-hydrogen and one atom of muriatic acid. Or in a state of vapour its constituents are

2 volumes olefiant gas = 1.94444 condensed into two 1 volume muriatic gas = 1.28472 condensed into two volumes; which gives 2.153 for the specific gravity, and this number does not differ much from 2.219 obtained by Thenard. If we admit its composition to be so, its constituents will be

4 atoms hydrogen	•	•	<b>0.5</b> .	or 6.15
4 atoms carbon	1		3.0	36.92
1 atom muriatic acid	•	•	4.625	<b>56</b> ·92
			8.125	99.99

These numbers appear at first sight to deviate enormously from those of Thenard; but the difference is only apparent. The

quantity of carbon approaches very nearly to that given by sect IV. When we correct the hydrogen by applying the more correct data which we at present possess, Thenard's number will approach much nearer to 6.15 per cent. than it does at To obtain the true quantity of muriatic acid, we must add the quantity of oxygen and muriatic acid found by Thenard together, because the supposed oxygen was deduced from an erroneous estimate of the atomic weight of muriatic acid. This will raise the amount of acid to 52.75 per cent. which does not differ much more than 4 per cent. from the calculated number. Even this difference would diminish, if we were to apply the exact data which we now possess to Thenard's experiment.

If the preceding estimate of the composition of muriatic ether be correct, it contains no water, and the combustible constituent can neither be considered as olefiant gas nor tetarto-carbo-hydro-gen. For it is a combination of 2 volumes of olefiant gas and I volume of muriatic acid gas combined, and condensed into 2 volumes.

### 2. Chloric Ether.

This compound was first noticed by Scheele\* and West-History. It has been since noticed by different chemists. rumb. Trommsdorf,+ Gehlen, Thenard, Berthollet, Robiquet and Colin, and Despretz, \*\* have made experiments on it in succession. Its nature has not yet been determined in a satisfactory manner; but I have noticed it here in order to draw to it the attention of experimental chemists. It has been frequently called heavy muriatic ether, from the supposition that the chlorine has been converted into muriatic acid.

It was prepared by passing a current of chlorine gas through Formation. alcohol or sulphuric ether, till these liquids refused to absorb any more. The alcohol acquired a yellowish-green colour, and a strong smell of muriatic acid. During the process some carbonic acid gas was evolved. When the process was terminated an oily looking fluid had precipitated to the bottom, and when the liquid swimming over it was saturated with potash, an additional portion of this oily matter made its appearance. When ether is employed the oily matter makes its appearance when the saturated liquid is mixed with water. It is to this

<sup>\*</sup> Opuscula, ii. 135.

t Gehlen's Jour. ii. 227.

Ann. de Chim. et de Phys. i. 426.

<sup>+</sup> Scherer's Jour. iii. 378.

<sup>§</sup> Mem. d'Arcueil, i. 147; ii. 25.

<sup>¶</sup> Ibid. ii. 299. \*\* Ibid. xxi. 437.

Chap. III. oily looking substance that the name of chloric or heavy muriatic ether has been given.

Properties.

It is a colourless, thin, oily looking fluid, having, according to Vogel, the specific gravity of 1.134. It is more volatile than water; has a smell somewhat similar to that of nitric ether, an aromatic, hot, and somewhat bitter taste. It does not redden litmus paper. It is very little soluble in water. Vogel added two drops of it to an ounce of water, and several days elapsed before they disappeared. But in alcohol and sulphuric ether it dissolves in any proportion. When assisted by heat it dissolves a little phosphorus.

It burns with a greenish-yellow flame, evolving muriatic Muriatic acid likewise makes its appearance when this substance is passed through a red-hot porcelain tube.

Nothing very precise has been determined respecting the composition of this ether. Despretz considers it as a compound of

1 volume chlorine.

I volume tetarto-carbo-hydrogen, or

2 volumes of olefiant gas.

But he has not established the truth of this opinion by any satisfactory experiments. It is clear from the experiments of Robiquet and Colin, that its properties are essentially different from the compound of I volume of chlorine and I volume of olefiant gas, which I distinguished in the last edition of this work (but improperly) by the name of chloric ether.

# 3. Hydrobromic Ether.

History.

This ether was first formed in 1827 by M. Serullas, and has been very imperfectly examined. It was prepared by the following process:

Formation

Forty parts of alcohol of the specific gravity 0.827 were put into a small tubulated retort, to this one part of phosphorus was added, and finally 7 or 8 parts of bromine were poured in by little at a time. Every time that bromine came in contact with the phosphorus under the alcohol, a rapid combination took place and heat was produced. Hence hydrobromic acid and phosphorous acid were formed. The mixture was now distilled by a gentle heat, what came over being received in a globular glass vessel well cooled. This product being mixed with water, the hydrobromic ether separated and sunk to the bottom.

Properties.

Hydrobromic ether thus prepared is colourless and transparent, heavier than water, has a strong etherial smell, a sharp taste, and is very volatile. It is soluble in alcohol, from which sect. IV. it is precipitated by water. It does not alter its colour by keeping.\*

# 4. Hydriodic Ether.

This ether was discovered by M. Gay-Lussac. He formed History. it by mixing together 2 volumes of absolute alcohol and 1 volume of hydriodic acid, of the specific gravity 1.7, and distilling in a water-bath. He obtained an alcoholic liquid perfectly neutral, colourless, and limpid. When mixed with water, a liquid precipitated in small globules, at first milky, but which gradually became transparent. This liquid was hydriodic ether. What remained in the retort was hydriodic acid, much coloured by an excess of iodine.

Serullas formed it by the same process as that which furnished hydrobromic ether; by adding iodide of phosphorus to alcohol in a tubulated retort, and distilling the mixture. The ether was separated from the alcoholic liquid in the receiver by water.+

Hydriodic ether, after being well washed with water, is per-properties, fectly neutral. Its odour is strong, and, though peculiar, it is analogous to that of other ethers. In a few days it acquires a reddish colour, which does not increase in intensity. Mercury and potash instantly destroy this colour by removing the iodine to which it is owing. Its specific gravity, at 72°, is 1.9206. It boils at the temperature of 148°½. It is not inflammable, but merely gives out purple vapours when put upon burning coals. Potassium may be kept in it without alteration. Potash does not alter it immediately, neither do nitric, and sulphurous acids, or chlorine. Sulphuric acid renders it instantly brown. When passed through a red-hot tube, it is decomposed, an inflammable carburetted gas is obtained, hydriodic acid evolved, and some charcoal deposited.‡

This ether has not been analyzed; but analogy would lead to the opinion that it is a compound of

1 volume iodine vapour,

1 volume tetarto-carbo-hydrogen, or

2 volumes of olefiant gas.

On that supposition its atomic weight will be 19.375. And it will be a compound of 10 atoms.

<sup>\*</sup> Ann. de Chim. et de Phys. xxxiv. 99-

<sup>†</sup> Ibid. xxv. 323.

<sup>†</sup> Ann. de Chim. xci. 89.

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Muriatic, hydrobromic, and hydriodic ethers are probably analogous compounds, consisting of 4 atoms carbon and 4 atoms hydrogen (whether in the state of olefant gas or tetarto-carbohydrogen is doubtful), united respectively with an atom of muriatic acid, hydrobromic acid, and hydriodic acid. They contain no water, and in this important circumstance differ from the eight following ethers, which seem, like sulphuric ether, to contain water as an essential constituent.

# 5. Sulphocyanic Ether.

History.

This ether was discovered by M. Liebig, and described by him in a Memoir published in 1829.\* It was obtained by distilling a mixture of 1 part of sulphocyanodide of potassium, 2 parts of sulphuric acid, and three parts of ether of the specific gravity 0.848. The product of the distillation being mixed with water, an oleaginous liquid separated, the weight of which was about \$\frac{3}{4}\$ths of that of the sulphocyanodide employed. At first it swam on the surface, but the alcohol and sulphuric ether which it contained, being removed by repeated washings, it sunk to the bottom under the form of a colourless or slightly yellowish oil.

Properties.

It has a strong smell of assafœtida or cochlearia officinalis, which adheres strongly to every thing which it touches. It is insoluble in water, but it communicates its odour to that liquid. It has a sweetish taste, and leaves an impression of peppermint in the mouth. It is very soluble in alcohol and sulphuric ether. It burns readily, and gives out fumes of sulphurous acid. It begins to boil at 151°, but the boiling point rises to 161°. Its alcoholic solution does not possess acid properties. It is not decomposed either by potash or ammonia.

Potassium placed in contact with it, after being rectified from dry chloride of calcium, preserves its lustre for some time; but if heat be applied it becomes covered with a yellow crust soluble in water, and precipitating peroxide of iron red. Hence the crust was sulphocyanodide of potassium.

Nitric acid acts upon it with great violence, producing even combustion. Much deutoxide of azote is given out, and the remaining liquid contains sulphuric acid. This ether absorbs chlorine abundantly, sulphuretted hydrogen gas is given out, and the smell of chloride of sulphur becomes sensible. If we add water, and continue to pass chlorine gas, more of it is

absorbed, and the smell of chloride of cyanogen becomes perceptible. The liquid is now acid, and precipitates barytes salts.

Iodine dissolves readily in this ether. Sulphur is also very soluble in it if we elevate the temperature. The same remark applies to phosphorus.

Though this ether has not been analyzed, yet it is evident that it contains sulphocyanogen, and that it is destitute of water, and analogy leads to the opinion that it is a compound of 1 integrant particle of sulphocyanogen, and 1 integrant particle of tetarto-carbo-hydrogen united together.

#### 6. Nitric Ether.

Nitric ether is first mentioned in an epistle written by Kunkel History. to Voight, and published in 1681;\* but no attention was paid to it by succeeding chemists till it was discovered a second time by Navier in 1742,† and a third time by Sebastiani in 1746.‡

The method of preparing it, proposed by Navier, was this: Twelve parts of alcohol are put into a strong bettle, which is kept surrounded with water, or rather with ice; eight parts of nitric acid are poured in at intervals, the mixture being agitated after every addition. The bottle is then well corked, and the cork secured by leather. Ether gradually forms at the surface of the liquid. After five or six days, when the formation is supposed to be over, the cork is to be pierced with a needle, to allow a quantity of nitrous gas to escape, which would otherwise carry the ether along with it. The cork is then to be drawn; the whole liquid is to be poured into a funnel, and by means of the finger the liquid below is allowed to run out while the ether is retained.

This method is somewhat hazardous; for the quantity of nitrous gas evolved is so great as often to burst the bottle. Dr. Black substituted in place of it a very ingenious process. He put into a glass phial the proper quantity of nitric acid; over this was poured gently a stratum of water, and the alcohol was poured over all. Thus there were three strata of liquids in the vessel: the acid lowermost, and the alcohol uppermost, separated from each other by the water. The acid and alcohol gradually combined with the water, and coming into contact acted on each other without violence; and thus the ether was formed without risk.

Dehne has given another process for obtaining nitric ether

<sup>\*</sup> Epistola contra Spiritum Vini sine Acido.

<sup>†</sup> Mem. Par. 1724. ‡ Diss. de Nitro, 1746.

Chap. III. exceedingly tedious, but not attended with any risk. The alcohol is put into a tubulated retort, to which a large receiver is luted; 1/48th part of nitric acid is to be added every four hours, drop by drop, till it amounts to about half the weight of alcohol; then the mixture becomes hot, and the ether passes over into the receiver. After this a little more nitric acid is to be added every morning and evening. Ether gradually forms on its surface. The acid is to be added till it falls down to the bottom of the retort in the form of green globules, indicating the perfect saturation of the acid with nitrous gas. This is a proof that no more ether will be formed.

> Various other methods of preparing nitrous ether have been proposed by chemists, as the distillation of a mixture of sulphuric acid, nitre, alcohol, &c. But the process preferred by artists is that of Chaptal as corrected by Proust. A large retort is luted to a glass globular vessel furnished with a tube of safety. From this globe a tube passes to a second, likewise furnished with a tube of safety; and to this last vessel is connected three Woolfe's bottles in the usual way, which must be half full of alcohol. A mixture of 32 parts of alcohol and 24 of acid, of the specific gravity 1.3, is put into the retort. The heat of a chaffing dish is applied, and removed as soon as the effervescence begins. The greatest part of the ether is detained by the alcohol in the first Woolfe's bottle. This mixture is to be saturated with an alkali, and the ether separated by distillation.\*

> These processes are all of them so defective and complicated, that little precise knowledge was acquired of nitric ether, till Thenard undertook an investigation of it in 1807. He distilled a mixture of alcohol and nitric acid, and carefully collected and examined all the products both liquid and gaseous. siderable part of the ether formed he found made its escape in the gaseous form, while the liquid in the receiver, hitherto considered nitric ether, was a mixture of alcohol, water, ether, nitrous, and acetic acids. These results led him to the following method of procuring pure nitric ether:

<sup>•</sup> Proust, Ann. de Chim. xlii. 262.—Brugnatelli has proposed the following method; but I find that the proportion of ether obtained by it is much smaller than the other processes, though Brugnatelli affirms the reverse. Put an ounce of sugar into a retort, and pour over it two ounces of alcohol. Lute to it a large receiver with slips of paper, and then add three ounces of nitric acid. The sugar is dissolved, the mixture boils, and the ether passes over pure, equal in weight to the alcohol. See Jour. de Chim. iii. 68. haps\_my want of complete success was owing to the use of a stronger acid than that employed by Brugnatelli.

Equal weights of alcohol and nitric acid, of the specific gravity
1.283, were put into a retort. To the beak of the retort was formation.

luted a glass tube, which was plunged to the bottom of a long narrow glass jar half filled with a saturated solution of common salt in water. From the top of this jar passed another tube, which went to the bottom of another similar jar, likewise half filled with a solution of common salt. In this manner five similar jars were connected with each other, each half filled with a saturated solution of common salt. From the last a tube passed to a water trough to receive the gaseous products in proper jars. Each of these five jars was surrounded with a mixture of snow and salt to keep it as cool as possible. moderate heat being applied to the retort a violent effervescence It was found necessary to withdraw the fire, and even to moisten the outside of the retort with water, in order to prevent the vessels from bursting. The gaseous matter evolved was thus forced to pass through the different jars containing the common salt solution, and there it deposited the greatest part of its ether. The ether was found floating on the surface of the solutions in each, but the greatest part of it in the first jar. It was separated; and to free it from the nitrous and acetic acids with which it was contaminated, it was agitated in a close phial with a sufficient quantity of chalk, till it ceased to produce any change on vegetable blues. It was then decanted off. The properties of this ether are as follows:

It has a slightly yellow colour, and a very strong ethereal Properties. odour. Its taste is strong and quite peculiar. It is rather heavier than alcohol, but much more volatile than sulphuric ether. Hence it only moistens bodies for a moment, and produces a very considerable degree of cold by its evaporation. The heat of the hand is sufficient to set it a boiling.

The specific gravity of its vapour, as determined by Dumas and Boullay, is 2.627, that of air being reckoned unity.\*

It is lighter than water, and requires 48 parts of that liquid to dissolve it, and communicates to it an odour like that of apples. It dissolves in alcohol in every proportion. It burns very brilliantly with a white flame like sulphuric ether. When kept for some time, both nitrous and acetic acids are formed in The same acids are evolved if the ether is heated, or if it be agitated with water. When brought in contact with a little of these acids, it instantly absorbs them, and acquires the property of converting vegetable blues into red.

<sup>\*</sup> Ann. de Chim. et de Phys. xxxvii. 31.

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When brought in contact with deutoxide of azote, or any other gas, at the temperature of 70°, it instantly quintuples its bulk, being converted into vapour. At that temperature its vapour is capable of supporting a column of mercury 28.74 inches high. At the temperature of 70°, and when the barometer stands at 30 inches, it is liquid; but if we increase the heat or diminish the pressure, it assumes the state of vapour. It is much more elastic than sulphuric ether. At the temperature of 70°, the vapour of sulphuric ether is capable of sustaining a column of mercury only 16 inches high.

It was subjected to a careful analysis by Thenard, by passing it through a red-hot porcelain tube, and examining the new substances evolved. They were water, carbonic acid, charcoal, oil, and a considerable quantity of gas which contained azote and nitrous gas, and a heavy inflammable air, which detonated with oxygen, and yielded carbonic acid and water. A little ammonia appeared also to have been produced. By estimating the weight of each of these substances and their constituents, Thenard concluded, that 100 parts of nitric ether was composed of

48·52 oxygen 28·45 carbon 14·49 azote 8·54 hydrogen

#### 100.00\*

In 1828 it was subjected to a new analysis by MM. Dumas and Boullay, by passing it through red-hot black oxide of copper, and collecting the azotic gas, carbonic acid gas, and water evolved, and estimating the oxygen by subtracting the loss of weight from abstraction of oxygen from the black oxide from the oxygen in the carbonic acid and water formed. The result of four different analyses made in this way with great care, gave the constituents of the ether as follows:

Composition.

Carbon			32.69
	•	•	
Azote	•	•	19.00
Hydrogen	• `	•	<b>6</b> ·8 <b>5</b>
Oxygen	•	•	41.46
,0			

100.00+

Now these respective weights are proportional to

<sup>&#</sup>x27;\* Mem. d'Arcueil, i. 360. + Ann. de Chim. et de Phys. xxxvii. 24.

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4.02 atoms carbon,

1 atom azote,

5.06 atoms hydrogen,

3.82 atoms oxygen.

We can have no hesitation, therefore, in considering the constituents as

4 atoms carbon, 5 atoms hydrogen, 1 atom azote, 4 atoms oxygen.

Now these are equivalent to

1 atom tetarto-carbo-hydrogen { 4 atoms carbon, 4 atoms hydrogen. 1 atom water { 1 atom hydrogen, 1 atom oxygen. 1 atom azote, 3 atoms oxygen.

But sulphuric ether is a compound of 1 atom tetarto-carbohydrogen and one atom of water. We may, therefore, consider nitric ether as a compound of

> 1 atom sulphuric ether, 1 atom hyponitrous acid.

Its atomic weight, therefore, must be 8.25.

Let us see how nearly the specific gravity of the vapour of nitrous ether tallys with this view of its constitution. We have seen that this specific gravity was found to be 2.627.

2)5.2083

2.60415

If we consider it as a compound of 1 volume of sulphuric ether vapour, and 1 volume of hyponitrous acid vapour combined together without any condensation of volume whatever, the specific gravity of its vapour would be 2.60415, for that is the mean between the specific gravity of sulphuric ether vapour and that of hyponitrous acid vapour. Now 2.60415 differs from 2.627, the specific gravity as determined by Dumas and Boullay by less than one per cent. There seems, therefore, no reason to hesitate about the view of the constitution of this ether first

<sup>\*</sup> Obtained by multiplying 4.75 (the atomic weight of hyponitrous acid by 0.5555.

suggested by these chemists; namely, that it is a compound of an atom of sulphuric ether, with an atom of hyponitrous acid.

## 7. Oxalic Ether.

History.

This ether was first noticed by Bergman,\* and afterwards by Thenard† and Bauhof.‡ More lately it has been accurately examined and analyzed by Dumas and Boullay.§

Formation,

The process of Dumas and Boullay, by which they procured this ether readily and in abundance, was as follows: A mixture of 1 part alcohol, 1 part binoxalate of potash, and 2 parts of sulphuric acid, was distilled. There came over first alcohol, then sulphuric ether, and at last an oleaginous liquid, which collected at the bottom of the receiver. The distillation may be continued till all the alcohol has been driven out of the retort. The last portions are richest in oxalic ether. oleaginous liquid is the one which contains that liquid. alcohol floating on its surface was removed by decantation, and the oily liquid was poured into a tall jar containing water. first the oily liquid floated on the surface, but in proportion as the sulphuric ether which was mixed with it evaporated, it fell in large drops to the bottom of the vessel. If we pour the alcoholic liquid into the retort, or add a new dose of alcohol, more oxalic ether will come over. A third dose of alcohol will still vield it, but in less quantity.

The oxalic ether thus obtained was acid, and it contained water, alcohol, and sulphuric ether. To purify it it was boiled with powdered litharge, and the boiling was continued till the boiling point, which was at first 194°, rose as high as 263°. By continuing this heat the whole water, alcohol, and sulphuric ether, evaporated, while the uncombined acid united with the litharge and was removed. The oxalic ether was now poured into a dry retort and distilled over.

Properties.

Its properties, when thus purified, are as follows: It is an oleaginous liquid having a specific gravity of 1.0929 at the temperature of 45°.5. It boils at 263°. Its smell is aromatic, but has something analogous to that of garlic or phosphorus.

The specific gravity of the vapour of oxalic ether, as determined by Dumas and Boullay, is 5.087, that of air being reckoned unity.

<sup>\*</sup> Opuscula, i. 256. † Mem. d'Arcueil, ii. 11.

<sup>‡</sup> Schweigger's Jour. xix. 308.

<sup>§</sup> Ann. de Chim. et de Phys. xxxvii, 21.

It was analyzed a great number of times by Dumas and Boullay, by the same process as they followed in the analysis of nitrous ether. The results were as follows:

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									Mean,	
Carbon	•	•	49.61	•		48.95	•		49.28	Composition.
Oxygen	•	•	43.77	•		44.09	•	•	43.93	
Hydrogen	•	•	6.62	•	•	6.96	•	•	6.79	
			100.00			100.00			100.00	

These numbers are proportionable to

5.984 atoms carbon, 4 atoms oxygen,

4.94 atoms hydrogen.

It is obvious from this that the true constituents must be

6 atoms carbon,

4 atoms oxygen,

5 atoms hydrogen.

Dumas and Boullay showed that oxalic acid exists as a constituent of this ether by actually separating it. Now, an atom of oxalic acid is composed of

2 atoms carbon,

3 atoms oxygen.

If we subtract these atoms from the constituents of oxalic ether, there remain

4 atoms carbon,

5 atoms hydrogen, 1 atom oxygen.

Now, these are the very constituents of sulphuric ether, which, as we have seen before, may be resolved into

1 atom water . . { 1 atom hydrogen, 1 atom oxygen. 4 atoms hydrogen, 4 atoms carbon.

Thus it appears that an integrant particle of oxalic ether is a compound of 1 atom of oxalic acid and one atom of sulphuric ether, so that its atomic weight is 9.125.

Let us see how this constitution will agree with the specific gravity of the vapour of oxalic ether as determined by Dumas and Boullay. The reader will recollect that it is 5.087. Now, the specific gravity of sulphuric ether vapour is 2.5694, and that of oxalic acid vapour must be 2.5.\* We have therefore

<sup>\*</sup> Obtained by multiplying its atomic weight by 0.5555.

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5.0694

5.0694 agrees so nearly with 5.087, the experimental result, that there seems no reason to doubt that this ether in the state of vapour is a compound of 1 volume of sulphuric ether and 1 volume of oxalic acid vapour, condensed into 1 volume.

Analysis,

Dumas and Boullay analyzed this ether by means of potash-7.348 parts of oxalic ether left for 24 hours in contact with a strong solution of caustic potash were completely decomposed. It was now introduced into a retort containing dry carbonate of potash, and distilled. 18.277 parts of a liquid were obtained of the specific gravity 0.970 at 50°. So that it contained 0.25 of absolute alcohol. Hence 100 parts of oxalic ether yielded 62.18 parts of absolute alcohol. From the same quantity of the ether 48.98 parts of oxalic acid were obtained. Thus the constituents from this mode of analysis were (supposing 100 parts of oxalic ether)

Oxalic acid	•	•	48.98
Alcohol .	•	•	62·18
			•
			111.16

It may at first sight seem enigmatical that the weight of the constituents should exceed that of the ether by 11·16 per cent. The reason is, that the sulphuric ether in the oxalic ether became alcohol during the decomposition. The sulphuric ether in 100 parts of oxalic ether was 51·02. Now 51·02 parts of sulphuric ether if converted into alcohol would become about 63 parts, which comes very nearly to the quantity of alcohol obtained in the experiment of Dumas and Boullay above detailed.

When a current of ammoniacal gas was passed through oxalic ether it underwent decomposition, but in a way very different from what was expected. One-half of the tetarto-carbo-hydrogen of the sulphuric ether entered into combination with the oxalic acid, and formed a new acid, similar in its nature to the sulphovinic acid, and which therefore may be called oxalovinic acid. This new acid possesses a saturating power only half as great as that of oxalic acid. It was saturated with ammonia. Hence the oxalovinate of ammonia formed was a compound of

Oxalovinic acid . . . 12.5 or two atoms, Ammonia . . . . 2.125 or one atom.

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The other half of the tetarto-carbo-hydrogen reduced to the state of olefiant gas united to an atom of water and constituted alcohol, which was easily separated by distillation, and its quantity determined. 100 parts of oxalic ether treated in this way gave out 31.48 parts of alcohol, which is only the half of the quantity furnished by it when it is decomposed by potash.\*

# 8. Acetic Ether.

This ether was discovered by the Count de Lauraguais in Tistory. 1759.† He obtained it by distilling a mixture of acetic acid and alcohol, with the same precautions as are employed in the distillation of sulphuric ether.

The process, as corrected by Pelletier, is as follows: Mix Preparation. together in a retort equal quantities of concentrated acetic acid and alcohol, and distil over the alcohol. Pour it back into the retort, and distil a second time. What comes over must be poured back a second time, and subjected to a third distillation. The product of this third distillation is a mixture of acetic acid and ether. Saturate the acid with potash, and distill with a moderate heat. Acetic ether comes over pure.‡ Bucholz has given another process, which is much more economical. Put into a retort 16 parts of acetate of lead, 6 parts of strong sulphuric acid, and 9 parts of alcohol. Distil over 10 parts. Agitate this liquid with a third of its bulk of lime-water, and decant off the ether, which will swim on the surface. It usually amounts to 6 parts.§

Scheele could not succeed in obtaining ether by Lauraguais' process; most likely because he neglected to return the distilled liquid a sufficient number of times into the retort. But he discovered another, by which it may be obtained without difficulty. Nothing more is necessary than to add a little sulphuric acid to the mixture; or acetic ether may be obtained by dissolving one part of acetate of potash in three parts alcohol, adding more sulphuric acid than is sufficient to saturate the potash, and then distilling.

Schulz, an apothecary at Kiel, repeated the experiments of Scheele, and found them accurate. His experiments were

<sup>\*</sup> See Dumas and Boullay; Ann. de Chim. et de Phys. xxxvii. 21, 30, 33, 34.

<sup>†</sup> Jour. de Scav. 1759, p. 324.

<sup>‡</sup> Jour. de Phys. xxviii. 141.

<sup>§</sup> Jour. de Chim. iii. 222.

Scheele, ii. 117.

Chap. III. repeated by Gehlen and Lichtenberg with the same result. They affirm that pure acetic acid does not form ether with alcohol, but that ether is formed if there be present the smallest quantity of any other acid.\* The subject has been lately examined by Henry† and by Thenard,‡ both of whom have shown in the most satisfactory manner that acetic acid and alcohol yield an ether by the process of Lauraguais and Pelletier.

Thenard employed nearly equal weights of a very strong acid and alcohol of the specific gravity 0.8056, and repeated the distillation 12 times. No gas of any kind was evolved during the process. He then mixed the whole together, and endeavoured to neutralize the acetic acid by potash. The neutrallization succeeded but imperfectly; abundance of crystals of acetate of potash precipitated. By a cautious distillation the acetic ether came over in the first place, and afterwards a portion of alcohol, holding a little ether and acetic acid in solution. By a subsequent distillation off acetate of potash, the acetic ether was obtained perfectly pure. During the formation of this ether, a quantity of acid as well as of alcohol disappear; both of course enter into the composition of the ether, or at least their constituents enter.

Dumas and Boullay, who examined this ether in 1828, formed it by distilling 15 times a mixture of equal weights of concentrated acetic acid and alcohol, pouring back the liquid The ether thus obtained into the retort after each distillation. was mixed with alcohol, from which they freed it by washing it with water. No fewer than 15 washings were required. These so reduced the quantity of the ether that enough was not left to enable them to determine its specific gravity.

Properties.

Acetic ether is limpid and colourless: it has an agreeable odour of ether and acetic acid. It does not redden vegetable It has a peculiar taste different from that of all other substances, and bearing no resemblance to that of alcohol. specific gravity, at the temperature of 44° 1, is 0.866, as determined by Thenard; and 0.882, at the temperature of 64°, as determined by Gehlen. No doubt weight in the case of this ether is a test of purity; we may therefore consider Gehlen's estimate as nearest the truth. Its boiling point, as determined by Dumas and Boullay, is 165°. The specific gravity of its vapour is 3.067. It burns with a yellowish-white flame, and acetic acid is developed during its combustion. It does not

<sup>\*</sup> Ann. de Chim. lvii. 94. + Ibid. lviii. 199. + Mem. d'Arcueil, i. 153.

undergo any change by keeping. At the temperature of 62° it requires more than seven times its weight of water to dissolve it.

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Though allowed to remain in contact with water, or dissolved in it, no change takes place, but when left in contact with caustic potash, acetic acid is gradually evolved, which saturates the alkali. If it be distilled in this state, alcohol comes over very much diluted with water. No gaseous matter is disengaged.

It was analyzed by Dumas and Boullay in the same way as nitrous and oxalic ethers. They obtained the following con-

stituents:

	•		1.			2.			Mean.	
Carbon	•	•	54.820	•	•	53.06	•	•	<b>53.95</b> °	Composition.
Oxygen	•	•	$36 \cdot 425$	•	•	38.25	•	•	37.33	
Hydrogen	1	•	8.755	•	•	8.69	•	•	8.72	
			100.000			100.00			100.00*	

These weights are equivalent to the following atomic constituents:

7.74 atoms carbon,

4 atoms oxygen,

7.42 atoms hydrogen.

These come sufficiently near

8 atoms carbon,

4 atoms oxygen,

7 atoms hydrogen,

to leave no doubt that these atoms represent the true constitution of the other.

But I have shown formerly that acetic acid is a compound of

2 atoms hydrogen,

4 atoms carbon,

3 atoms oxygen.

If we subtract these atoms from the numbers in the preceding table, there will remain

5 atoms hydrogen,

4 atoms carbon,

l atom oxygen.

Now, it has been already shown that these are the constituents of sulphuric ether. Thus it appears that acetic ether, like the two preceding, is a compound of an integrant particle of acetic acid and an integrant particle of sulphuric ether. Its atomic weight, therefore, is 10.875.

<sup>\*</sup> Ann. de Chim. et de Phys. xxxvii. 27.

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Let us see how well the specific gravity of its vapour will correspond with this constitution. This was determined by Dumas and Boullay to be 3.067. Now

<ol> <li>volume sulphuric ether</li> <li>volume acetic acid vapour</li> </ol>	•	•	•	2·5694 3·4722
			•	2 6.0416

3.0208

If we consider it as a compound of 1 volume of sulphuric ether and 1 volume of acetic acid vapour united together without any diminution of volume, the specific gravity will be 3.0208. This comes within one per cent. of the determination of Dumas and Boullay, and may therefore be considered as agreeing with it. There seems therefore no reasonable doubt that the constitution of this ether agrees with that of the two last, namely, that it is a compound of 1 atom acetic acid with 1 atom of sulphuric ether.

## 9. Benzoic Ether.

History.

This ether was discovered by Scheele.\* It was afterwards slightly examined by Thenard,† and more particularly by Dumas and Boullay.‡

Preparation.

The process of Scheele, as modified by Thenard, is the one which is usually followed. It consists in distilling a mixture of 4 parts of alcohol, 2 parts of benzoic acid, and 1 part of muriatic acid, till half the liquid has passed over. It is then poured back, and the process repeated. This distillation is renewed two or three times. The greatest part of the ether exists in the liquid remaining in the retort. It is separated by means of water, and two or three washings deprive it of the greatest part of its excess of acid. If we boil it on powdered litharge till the boiling point become fixed, and till all the excess of acid which it contains is saturated, and afterwards distil it over with caution, we obtain it in a state of purity.

Properties.

Thus prepared, it is a colourless oily-looking fluid. It has a weak smell, somewhat like that of benzoic acid. Its taste is pungent; its specific gravity at 51° is 1.0539, and its boiling point is 408° as determined by Dumas and Boullay. The specific gravity of its vapour, according to the same chemists, is 5.409. It was subjected to analysis by them in the same

<sup>\*</sup> Opuscula, ii. 141. † Mem. d'Arcueil, ii. 8.

<sup>‡</sup> Ann. de Chim. et de Phys. xxxvii. 20.

Composition.

way as the three preceding ethers. They obtained the follow- sect. IV.

ing as its constituents:

 Carbon
 .
 .
 73·32

 Oxygen
 .
 .
 19·10

 Hydrogen
 .
 7·87

100.29

Now these weights of these elements represent the following atoms of each:

20.46 atoms carbon,

4 atoms oxygen,

13.2 atoms hydrogen.

But if we were to consider benzoic ether as a compound of

19 atoms carbon,

4 atoms oxygen,

11 atoms hydrogen,

then the weight of each of these constituents in 100 parts of the ether would be

Now, the deviation of these numbers from those found by experiment, is not greater than frequently occurs in such experiments. The analogy of the three preceding ethers gives so much probability to these numbers, that Dumas and Boullay have adopted them as more accurate than their own. Let us see what the constitution of benzoic ether will be, admitting its atomic constituents to be as above stated. It has been shown in a preceding part of this volume that benzoic acid is a compound of

6 atoms hydrogen,

15 atoms carbon,

3 atoms oxygen.

If we subtract these atoms from the preceding table, there will remain

4 atoms carbon,

5 atoms hydrogen,

1 atom oxygen.

But these are the constituents of sulphuric ether. It follows, therefore, that benzoic ether, like the three preceding, is a compound of 1 integrant particle of benzoic acid, and 1 integrant particle of sulphuric ether. Its atomic weight then is 19.625.

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Let us see how the specific gravity of its vapour accords with this view of its composition. It was found to be 5.409. Now

> 2 10·9027 5·4513

If we consider it as a compound of 1 volume of sulphuric ether vapour, and 1 volume of benzoic acid vapour, united together without diminution of volume, the specific gravity will be 5.4513. Now this does not differ so much as one per centfrom the experimental result of Dumas and Boullay. This coincidence seems to leave no doubt that the constitution of benzoic ether is really as above determined.

### 10. Formic Ether.

History.

This ether was first formed by Arvidson in 1777, but only in an impure state. Bucholz\* examined it anew in 1782, and Gehlen+ prepared it in a state of greater purity, and determined its properties, in 1812.

It was obtained by Gehlen by the following process: Equal weights of absolute alcohol and concentrated formic acid were distilled in a retort to dryness. The product was distilled a second time; and the liquid in the receiver being mixed with a weak solution of potash, the formic ether separated, amounting to about four-fifths of the alcohol employed.

Properties.

This ether is a colourless liquid, which has a strong smell of peach kernels, yet Gehlen and Rose could find no trace of hydrocyanic acid in it. Gehlen compares the taste also to that of peach kernels. Its specific gravity, as determined by Gehlen, is 0.9157. It boils when heated to 133°. At the temperature of 73° the elasticity of its vapour is capable of supporting a column of mercury 8.74 inches in height, according to the determination of Dobereiner.‡ It burns with a bluish flame inclining to yellowish white. At the temperature of 55° it requires 9 times its weight of water to dissolve it. It dissolves readily in alcohol, and is separated again by the addition of water.

According to Dobereiner, it contains 44.2 per cent. of formic ether. Though this ether has not yet been subjected to

<sup>• \*</sup> Crell's Neueste Entdeck, vi. 55. † Schweigger's Jour. iv. 14. † Gilbert's Annalen, lxxiv. 416.

analysis, there can be little doubt, from the analogy of the four preceding ethers, that it is a compound of 1 integrant particle of formic acid, and 1 integrant particle of sulphuric ether.

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### 11. Tartaric Ether.

This ether was first prepared by Scheele;\* it was examined History. also by Thenard, but he did not succeed in procuring it in a state of purity.†

It was prepared by distilling a mixture of 6 parts of tartaric acid, and 7 parts of absolute alcohol, and 2 parts of sulphuric acid, until ether began to be formed. The process was the 1 stopped: on cooling it assumed the appearance of a thick syrup from which water did not separate any ether. It was then mixed with potash: much bitartrate of potash fell and was separated. The acid was then exactly saturated with potash, and the mixture digested in cold alcohol. The alcoholic liquid being evaporated, a liquid was obtained, which Thenard considered as tartaric ether.

It has a brown colour and a syrupy consistence, is slightly Proporties, bitter and disagreeable. It has no smell, and contains no excess of acid. It does not precipitate the solution of chloride of calcium, but it precipitates chloride of barium. It dissolves readily both in water and alcohol.

## 12. Citric Ether.

This ether was also first made by Scheele, ‡ and since his time has been examined by Thenard§ alone.

It may be prepared by a process similar to that which succeeds with oxalic ether. Its colour is yellowish; it is rather heavier than water, not very volatile, destitute of smell, and has a bitter taste. It is but little soluble in water, but dissolves readily in alcohol. When digested with potash, citric acid is separated from it.

# 13 . Malic Ether.

This ether, so far as I know, has been examined only by Thenard. The process is the same as for oxalic ether. It has a yellow colour, is somewhat heavier than water, is not volatile, and is destitute of smell. It is but little soluble in water, but very soluble in alcohol, from which it may be separ-

<sup>\*</sup> Opuscula, ii. 142.

<sup>†</sup> Opuscula, ii. 142.

<sup>|</sup> Ibid.

<sup>†</sup> Mem. d'Arcueil, ii. 13.

<sup>§</sup> Mem. d'Arcueil, ii. 12.

ated by the addition of water. When digested with potash malate of potash is formed.

These last three ethers, though they have not yet been analyzed nor obtained in a state of purity, present so many analogies with the preceding, that their constitution is probably the same, namely, a combination of an integrant particle of sulphuric ether with an integrant particle of the acid from which each derives its name.

### SECTION V.—OF ETHAL.

History.

• This substance was first obtained and described by Chevreul in 1818.\* I am induced to place it here on account of its analogy to alcohol and sulphuric ether in its composition. It was obtained by Chevreul from spermaceti.

Preparation.

The spermaceti was in the first place freed from a yellow oil which it contains, by repeated digestions and solutions in alcohol. The purified spermaceti (which Chevreul distinguishes by the name of cetine) was saponified by mixing 100 parts of it with 100 parts of potash dissolved in 200 parts of water, and keeping the mixture in a temperature varying between 122° and 194°, agitating it frequently. When the saponification is complete water is added, and an excess of tartaric or phosphoric acid, and sufficient heat is applied to dissolve the soap, and kept up till the fatty portion collects at the surface of the liquid.

The fatty matter thus collected weighs 101.6 parts. It has a light yellow colour, and begins to congeal at 113°, but is not quite solid till it be cooled to 110°, and it does not become quite hard till it reaches the temperature of 102°. This fatty matter is a mixture of ethal and margaric and oleic acids. These acidswere separated by heating it with barytes water, stirring it continually till the acids were saturated with barytes. The excess of barytes was then removed by boiling distilled water. The matter being now dried was digested in cold but very strong alcohol. The ethal was dissolved together with a little margarate and oleate of barytes. The alcohol being distilled off, and the residue treated with absolute alcohol or sulphuric ether, a solution of pure ethal was obtained. By the application of heat the solvent liquid was driven off, and the ethal remained in a state of purity.

Properties.

Ethal thus obtained is a solid colourless body, having the semitransparency of wax. It melts at about 118°, but when

\* Recherches Chimiques sur les corps grosses, pp. 161, 239.

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put into water it does not fuse till it has reached the temperature of 122°. When cooled slowly it crystallizes in brilliant plates, and sometimes radiated needles may be observed on its surface. It has no smell, and scarcely any taste. It may be volatilized at a temperature equal to that which is requisite to volatilize the fatty bodies which are destitute of acidity.

Alcohol of the specific gravity 0.812 dissolves it in any proportion at the temperature of 129°. But it is deposited partly in crystals when the solution cools. This solution has no action on vegetable colours. When ethal is heated with protoxide of lead no water is disengaged. It is insoluble in water: it does not combine with potash, nor form soap if it be pure, but if it be mixed with a small quantity of margaric or oleic acid, unites readily enough with potash, and is converted into a soap. Water deprives this soap of a great portion of its potash, and of part of its margaric and oleic acids, yet the residual matter, though consisting chiefly of ethal, forms a mucilage with water.

A compound of 60 parts of margaric and oleic acids which melts at 113°, and 40 parts of ethal, become liquid at 111°.

When ethal is heated sufficiently in an open vessel it burns like wax. Sulphuric acid has little action on it, unless it be assisted by heat. In that case sulphurous acid is formed, but most of the ethal remains undissolved. Nitric acid has little action on it cold, but when heat is applied much deutoxide of azote is given out, and the ethal is partly dissolved. The undissolved portion being treated with water, and the aqueous solution concentrated, acid crystals are obtained. Alcohol dissolves from the residue an oily matter.

Ethal was subjected to analysis by Chevreul, by means of black oxide of copper. He found the constituents by weight to be

Oxygen	•	•	6.2888
Carbon	•	•	79.7660
Hydrogen	•	•	13.9452

Composition.

100.0000

Now these weights are equivalent to the following atomic proportions:

1 atom oxygen, 8.99 atoms carbon, 17.7 atoms hydrogen;

numbers which approach very near

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1 atom oxygen, 9 atoms carbon, 18 atoms hydrogen.

The atoms of hydrogen are twice as numerous as those of carbon. If we were to admit one more atom of hydrogen than Chevreul found (and the quantity of hydrogen is always most liable to error in the determination), then ethal might be considered as a compound of

1 atom water

9 atoms carburetted hydrogen

1 bydrogen,

9 carbon,

18 hydrogen.

Chevreul is of opinion that the carbon and hydrogen bear the same ratio to each other in this substance as in alcohol and ether. This was the reason of the name *ethal* which he gave it, and which is formed by joining the first syllables of the words ether and alcohol together. But it is obvious that this supposed ratio does not hold, the atoms of hydrogen being twice as numerous as those of carbon.

#### SECTION VI. -- OF VOLATILE OILS.

The term oil is applied to a number of unctuous liquids, which, when dropped upon paper, sink into it, and make it seem semitransparent, or give it what is called a greasy stain. These bodies are very numerous, and have been in common use from time immemorial. Chemists have divided them into two classes; namely, volatile and fixed oils. We shall consider the properties of the first of these classes in this section. The fixed oils will occupy our attention in the next. A third class of oils might be added which possess intermediate properties between the fixed and the volatile.

Character of

Oil, what.

VOLATILE OILS, called also essential oils, are distinguished by the following properties:

- 1. Liquid; often almost as liquid as water; sometimes viscid or solid.
  - 2. Very combustible.
  - 3. An acrid taste and a strong fragrant odour.
- 4. Volatilized with water at a temperature not higher than 212°.
  - 5. Soluble in alcohol and ether, and slightly in water.
  - 6. Evaporate without leaving any stain on paper.
  - . By this last test it is easy to discover whether they have been

adulterated with any of the fixed oils. Let a drop of the vola- sect. VI. tile oil fall upon a sheet of writing paper, and then apply a gentle heat to it. If it evaporates without leaving any stain upon the paper, the oil is pure; but if it leaves a stain, it has been contaminated with some fixed oil or other.

Volatile oils are almost all obtained from vegetables, and they exist in every part of plants; the root, the bark, the wood, the leaves, the flower, and even the fruit, though they are never found in the substance of the cotyledons; whereas the fixed oils, on the contrary, are almost always contained in these bodies.\*

When the volatile oils are contained in great abundance in plants, they are sometimes obtained by simple expression. This is the case with the oil of oranges, of lemons, and of bergamotte; but in general they can only be obtained by distillation. The part of the plant containing the oil is put into a still with a quantity of water, which is distilled off by the application of a moderate heat. The oil comes over along with the water, and swims upon its surface in the receiver. By this process are obtained the oil of peppermint, thyme, lavender, and a great many others, which are prepared and employed by the perfumer. Others are procured by the distillation of resinous bodies. This is the case, in particular, with oil of turpentine, which is obtained by distilling a kind of resinous juice, called turpentine, that exudes from various species of pine.

Volatile oils are exceedingly numerous. They have been long known; but as their use in chemistry is but limited, they have not hitherto been subjected to an accurate chemical inves-M. Theodore de Saussure, however, has made numerous experiments to determine the composition of several of the most interesting volatile oils. They differ very much from each other in their properties; but it would serve no good purpose to enter upon a minute detail of each particular oil. I shall therefore satisfy myself with an account of their general properties, and then give an account of the characters of oil of turpentine, as a specimen of these oils.

1. The greater number of volatile oils are liquid, many indeed Consistence are as limpid as water, and have nothing of that appearance which we usually consider as oily. This is the case with the following; namely, oil of turpentine, oranges, lemons, berga-

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motte, roses. Others have the oily viscidity. It varies in them in all degrees. This is the case with the oils of mace, cardamom, sassafras, cloves, cinnamon. Others have the property of becoming solid. This is the case with the oils of parsley, fennel, aniseed, balm. Others crystallize by slow evaporation. This is the case with oil of thyme, peppermint, marjoram. The oil of nutmegs has usually the consistence of butter.\* This is the case also with the oil of hops and of pepper.

Colour,

2. The colour of the volatile oils is as various as their other properties. A great number are limpid and colourless, as oils of turpentine, lavender, rosemary, savine, aniseed. Some are yellow, as spike, bergamotte. Some are brown, as thyme, savory, wormwood. Others blue, as camomile, motherwort. Others green, as milfoil, pepper, hops, parsley, wormwood, cajeput, juniper, sage, valerian. Others, though at first colourless, become yellow or brown by age, as cloves, cinnamon, sassafras.+

Odour,

3. Their odours are so various as to defy all description. It is sufficient to say, that all the fragrance of the vegetable kingdom resides in the volatile oils. Their taste is always acrid, hot, and exceedingly unpleasant.

Specific gravity. 4. Their specific gravity varies very considerably, not only in different oils, but even in the same oil in different circumstances. The following are the specific gravities of several of the volatile oils, as ascertained by Dr. Lewis:

Oil of Sassafras .		1.094	Oil of Tansy	·946
Cinnamon		1.035	Carraway seeds	·940
Cloves .		1.034	Origanum .	·940
Fennel .		·997	Spike	·936
Dill **.		·994	Rosemary	·934
Pennyroyal		·978	Juniper berries	·911
Cummin .		·975	Lavender	.905€
Mint .		·975	Oranges	•888
Nutmegs .	•	<b>·94</b> 8	Turpentine .	·792

The following table exhibits the specific gravity of several volatile oils, as determined by M. de Saussure:

¶ Ann. de Chim. et de Phys. xiii. 259.

<sup>•</sup> Fourcroy, vii. 505. Eng. Trans. † Neuman's Chem. p. 272. ‡ Ibid. 

By my determination.

<sup>. ||</sup> Sometimes oil of turpentine is as high as 0.86.

Common oil of anise	*	. •	0.9857 at 78° sect vi.
Solid oil of anise	•	•	0.9849 at 78
Oil of lavender	•	•	0.898 at 68
Oil of rosemary	•	•	0.8386 at 60
Oil of turpentine	•	•	'0.86 at 71.5
Oil of lemons	•	•	0.847 at 71.5
Oil of roses	•	•	0.832 at 60
	•	•	

When the volatile oils are heated in the open air, they evaporate readily, and without alteration, diffusing their peculiar odours all around: but there is a considerable difference between the different oils in this respect. When distilled in close vessels, they do not so readily assume the form of vapour. they lose their odour, become darker in colour, and are partly decomposed. Oils do not seem very susceptible of assuming the gaseous form, unless some other substance, as water, bepresent.

The following table exhibits the elasticity of the vapour of Elasticity of their vapour, various oils, at the temperature of 59°, as determined by M. de Saussure.\* The elasticity is measured by the height of the column of mercury which the vapour is capable of supporting.

					Elast, at 59	<b>.</b>
Vapou	ur of water	•	•	•	0.507	inches mercury
Oil of	f turpentine	•	•		0.354	•
	lemons	•	•	•	0.354	
	rosemary	•	•	•	0.349	
	lavender	•	•	. •	0.310	
	roses	•	•	•	0.0787	7 *
	anise, common		•	•	0.059	
	anise, solid	•	•	•	0.0394	Ę

Oil of turpentine begins to boil in glass vessels at 314°. As the tension of oil of lemons is the same as that of oil of turpentine at 59°, the boiling point of both is probably the same. The other oils probably will not boil till they are raised to a considerably higher temperature.

When exposed to the action of cold, they congeal like the Action of cold. fixed oils; but the temperature necessary to produce this effect varies according to the oil. Some of them, as oil of anise and of fennel, become solid at the temperature of 50°: frozen oil of bergamotte and of canella become liquid at 23°; oil of turpentine at 14°.+ Margueron exposed several volatile oils to a cold of - 17°. They congealed or rather crystallized par-

† Margueron, Jour. de Phys. xlv. 136.

<sup>\*</sup> Ann. de Chim. et de Phys. xiii. 259.

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Action of light.

tially, and at the same time emitted an elastic fluid. These crystals consisted partly of the oils themselves, partly of other substances. Some of them had the properties of benzoic acid.\*

- 5. Volatile oils, when exposed to the action of light in close vessels, and excluded from common air, undergo very singular Their colour becomes deeper, they acquire a great deal of consistency, and their specific gravity is considerably The cause of these changes is but imperfectly known. Tingry, to whom we are indebted for these interesting researches, has proved that light is a necessary agent. was supposed formerly that they were occasioned by the absorption of oxygen; and when oxygen is present, it has been ascertained that it is absorbed: but Tingry has proved that the same changes go on when oxygen is excluded. This philosopher ascribes them to the fixation of light. If this be the real cause, the quantity of light fixed must be enormous; for as the specific gravity of the oils is increased considerably while the bulk continues the same, it is evident that the absolute weight must be increased proportionably. One circumstance, however, renders this conclusion somewhat doubtful, at least in its full extent; and that is, that the quantity of change was always proportional to the quantity of the oil and the quantity of air contained in the vessel.+
- II. It is probable that the volatile oils absorb and combine with the different supporters of combustion, though no correct set of experiments has been hitherto made on the subject.

Action of oxygen.

1. When volatile oils are exposed to the open air, they gradually become deeper coloured, and acquire more and more viscidity, while at the same time their odour diminishes. Dr. Priestley first ascertained that they imbibe oxygen with rapidity, and that the changes are owing to their absorption of it. He tried the experiment only with oil of turpentine, but he found that the air above oils of mint and cinnamon, confined in phials half full, was deprived of its oxygen.‡ He ascertained likewise, that, independent of this disposition to absorb oxygen, oil of turpentine has the property of imbibing a considerable quantity of air, which may be afterwards extricated by means of the air-pump.§ According to Fourcroy, this absorption of oxygen is accompanied by the formation of water. His evi-

Priestley on Air, ii. 232.

& Ibid.

<sup>\*</sup> Margueron, Jour. de Phys. xlv. 136.

<sup>†</sup> Tingry, Jour. de Phys. xlvi. 161 and 249.

dence for this is, that drops of water, he says, are often perceptible at the surface of those oils that are kept in vessels not properly closed.\* By long exposure the volatile oils assume the form of resins.

When the volatile oils are heated sufficiently in the open air, they take fire and burn with a clear bright flame, emitting a vast quantity of smoke. The products of the combustion, besides the soot, are water and carbonic acid.

- 2. Oil of turpentine at least absorbs and combines with chlo- of chlorine, rine, and the properties of the new compound are very different from those of oil of turpentine. Mr. Porrett caused the vapour of oil of turpentine and chlorine gas to pass together through a glass tube into a receiver. There was formed a very thick heavy white oil, which sank immediately in water, and which smelt and tasted very much like nutmegs, but communicated rather a more caustic sensation to the tongue. + A similar compound seems to have been obtained by Dr. John Davy by mixing perchloride of tin with oil of turpentine.
  - 3. The action of iodine on volatile oils has not been tried.
- III. The action of the simple combustibles upon the volatile oils is not remarkable. They do not absorb hydrogen as far as is known, neither are they altered by charcoal. When digested upon sulphur at the temperature at which the sulphur of sulphur, melts, they dissolve a portion of it, acquire a brown colour, and a disagreeable taste and smell. These preparations are called balsams of sulphur. A portion of the sulphur crystal-lizes as they cool.§ When these balsams are heated strongly, a vast quantity of gas, (probably sulphuretted hydrogen) is evolved so rapidly as to occasion very violent explosions, unless proper precautions be taken.

The volatile oils dissolve likewise a portion of phosphorus in of phospho. a digesting heat; but most of them deposite the whole of it again as the solution cools. Hoffman pointed out a method of rendering the solution permanent. It was the following: Triturate together 10 parts of camphor and 1 of phosphorus. This mixture dissolves readily in most volatile oils, as in oil of cloves, and forms a solution which has the property of rendering every

<sup>\*</sup> Fourcroy, vii. p. 501. Eng. Trans.

<sup>+</sup> Nicholson's Journal, xxxiii. 195.

Ibid. p. 17.

<sup>§</sup> Elemens de Chymie of Dijon Academy, iii. 357.

<sup>|</sup> Hoffman relates a remarkable story of the violent effects of such an explosion by way of caution to the chemists of his time. Observationes Phys. Chem. p. 308.

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thing luminous which is rubbed with it, and this without combustion.\* This seems to have been the solution so much used by Boyle, under the name of liquid phosphorus.

Action of alkalies and earths.

IV. The alkalies and earths act but feebly upon the volatile oils. The French chemists have proposed to give the combinations which these bodies form with the volatile oils the name of savonules, which Dr. Pearson has translated by the term saponules; but these denominations have not been adopted by chemists.+

Whoever considers the tedious trituration of potash and oil of turpentine together, by which the medicinal preparation called Starkey's soap is prepared, and compares it with the facility with which that alkali dissolves common turpentine, will be inclined to believe that the combination takes place only in so far as the oil is converted into a resin; and that it is not the oil which has the property of uniting with potash, but the resin formed by its absorbing oxygen from the atmosphere. Indeed it is not improbable, that the volatile oils absorb and part with oxygen, with much greater facility than has been hitherto supposed; and that during many of their solutions these changes take place. Volatile oils seem to unite to alkalies and earths only when united to oxygen so as to form resins; while resins, on the other hand, may probably owe their solubility in alcohol to their parting with oxygen, and assuming the state of volatile oils. Some experiments of Mr. Hatchett at least render the last supposition not improbable. I shall mention one: He took about half a pound of the common yellow resin of the shops, and having dissolved it in rather less than a quart of alcohol, he poured the clear solution from the dregs and impurities into a glass basin containing about two quarts of distilled water. He placed this basin on a sand-bath, and heated it moderately for about four hours. The principal part of the resin was precipitated during this digestion. Next day the milky liquor was poured off the precipitate, and evaporated to dryness in an open vessel. During the evaporation, brittle films of perfect resin were formed successively on the surface of the liquor, and the dry residue, after evaporation, was likewise complete resin; but the portion which had precipitated in the first basin, and which constituted the chief part of the original, was not in the state of resin, but of common turpentine.

\*.Hoffman, Observ. Phys. Chem. p. 307.

<sup>†</sup> The term saponule does not agree well with the idiom of our language. The word subscap, or something similar, would have been better.

These phenomena indicate in a very unequivocal manner, that Sect. VI. oxygen had been taken from the resin during its solution in Hence the portion which precipitated immediately when the solution was poured into water, not being in contact with the air, fell down in the state of turpentine; while the portion that continued in contact with air became perfect resin.

V. When agitated with water, the greater number of the Action of water, volatile oils render it milky, and communicate to it their peculiar odour. Several of them when dropped upon sugar, if the sugar be afterwards dissolved in water, form a permanent solution, to which the name of oleo-saccharum has been given. Margueron has shown that this property belongs only to the purest and most limpid part of the oils.

They are all soluble in alcohol, ether, and fixed oils; though they vary considerably in the facility with which they unite to alcohol. Oil of turpentine, for instance, is known to unite slowly with that liquid. When 1 part of that oil is dissolved in 7 parts of alcohol, the oil separates by degrees, and sinks to the bottom.\*

VI. The action of the acids upon the volatile oils has been but imperfectly examined.

Sulphuric acid acts upon them with considerable energy: of ulphuric dissolving them, converting them at first to a substance of a resinous nature, and at last reducing them to the state of char-Hence we may procure the oil in very different states, by separating it from the acid at the end of a longer or shorter interval by pouring the mixture into water. When a volatile oil is dropped very slowly into four times its weight of sulphuric acid, triturating constantly after every addition, a solution is formed of a brownish colour. If this solution is poured into 3 or 4 parts of water, and then gently heated, a brown mass separates, which was formerly known by the name of an acid soap. Achard is the only chemist who has examined these combinations with attention. His experiments were made chiefly on oil of turpentine. The mass which separates when this oil and sulphuric acid are treated as above described, is of the consistence of soft wax, soluble in water and alcohol; and when decomposed by an alkali, the oily matter which separates unites readily with alkalies. † Hence it appears that it has approached the state of a resin.

<sup>\*</sup> Neuman's Chem. p. 288.

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Muriatic acid has much less action on them than the sulphuric. From Achard's trials it dissolved  $_{120}$ th of its weight of the oil of sassafras. The portion dissolved is probably altered.\* With muriatic acid oil of turpentine combines and forms a compound very similar in its appearance to camphor.

When nitric acid is thrown upon them suddenly, and in a concentrated state, it acts with such energy as to set them on fire; but when sufficiently diluted with water it dissolves them, and converts them into a yellow substance similar to resin. Chlorine acts in the same way, though with less energy.

Action on metals.

VII. The action of the volatile oils on metals has not been examined with care, but it cannot be remarkable. Margueron has tried the effect of some of the salts of mercury upon several volatile oils. The following are the facts ascertained by this chemist: When oil of rosemary is kept over nitrate of mercury, the salt is gradually decomposed, and the oil acquires a deep Corrosive sublimate, in like manner, deepens the colour and increases the consistence of oils of citron, chevril, hyssop, lavender, rosemary, and peppermint; while it is at the same time partly converted into calomel. Neither the muriate of mercury, nor the sulphuret of that metal, produce any change in the oils of lavender and rosemary: but by this last oil the red oxide of mercury is converted into the black, though the oil does not experience any sensible change. The chloride of antimony is likewise decomposed by the oil of rosemary.+

Analysis of volatile oils,

M. de Saussure attempted the analysis of several of the volatile oils, by burning them in oxygen gas, and ascertaining the quantity of oxygen consumed, and the volume of carbonic acid formed. There are several circumstances which make it difficult to obtain very accurate results. The oils are so volatile that a portion is apt to escape combustion, and mingle with the gaseous products under the form of vapour. But the great obstacle to correct results, is the impossibility of freeing the oils from all foreign matter, and bringing them into a state of purity. Till some method of effecting this be devised, the analysis of the volatile oils cannot lead to any satisfactory conclusions. The following table exhibits the constituents of the different oils analyzed by Saussure:

<sup>\*</sup> Elemens de Chymie of the Dijon Academy, iii. 361.

<sup>†</sup> Ann. de Chim. xlvii. 66.

<sup>1</sup> lbid.

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·	Hydrogen.	· Carbon,	Oxygen.	Azote.	Total
Oil of lemons	12.326	86.899	0	0.775	100
turpentine	11.646	87.788	0	0.566	100
lavender	11.07	75.5	13.07	0.36	100
rosemary	9.42	82.21	7.73	0.64	100
roses	13.124	82.053	3.949	0.874	100
anise, common	9.352	76.487	13.821	0.34	100
ditto, solid	7.531	83.468	8.541	0.46	100

These weights give us the following atomic constituents of these oils:

	Hydrogen.	Carbon.	Oxygen,	Azote.
Oil of lemons	10	12	0	0.004
turpentine	10	13		
lavender	27	31	4	
rosemary	41	60	4.	
roses	53	<b>56</b>	2	
anise, common	11	15	2	
ditto, solid	14	26	2	

These atomic weights may be converted into volumes, simply by dividing the atoms of oxygen by 2, and allowing the others to remain unaltered. If we knew the specific gravity of the oils in a state of vapour, these volumes would enable us to form some idea respecting the constitution of the integrant particle of each oil; but our ignorance of that essential element prevents any other conclusion than what regards the ratio of the atoms of the hydrogen and carbon.

In oils of lemons, turpentine, lavender, and roses, the volumes of hydrogen and carbon approach equality. It is probable from this that in them the hydrogen and carbon are combined so as to make some modification of carbohydrogen; but how many atoms of each go to the formation of an integrant particle it is impossible to say, probably a much greater number than any of carbohydrogen hitherto examined, the highest of which is hexacarbohydrogen, or a compound of 6 atoms carbon and 6 atoms hydrogen into one volume.

Solid oil of anise seems to consist of a compound of 1 volume of hydrogen and 2 volumes carbon vapour, or some multiple of that. It is therefore analogous to one of the oils from oil gas which was subjected to analysis by Mr. Faraday.

Oil of rosemary and common anise appear to be a compound

Chap. HL of 1 volume hydrogen and 11 volume carbon vapour, or some multiple of that. It is therefore analogous to naphthaline.

The oxygen enters into these bodies in very small quantity. In lavender and rose oils it is probably united to carbon, but in oils of rosemary and common anise, and in solid anise oil, it seems to be united to hydrogen and to constitute water. The presence of azote was inferred by Saussure from the appearance of a little ammonia during his analysis of the different oils. Its quantity is so small, that if it enters as an atomic compound, the number of atoms of the other constituents must be prodigious. Thus, if oil of lemons contain an atom of azote, it must be a compound

> 224 atoms hydrogen, 263 atoms carbon, 1 atom azote.

Of the nature of so very complex an integrant particle as this it is difficult to form any conception. I think it quite conceivable that the ammonia may have originated from the presence of a little azotic gas in the oxygen gas employed in the combustion of the oils. At any rate, its quantity is so small, that in the present state of our knowledge it may be neglected.

Oil of lemons and oil of turpentine appear to contain no oxygen, but that principle enters as a constituent into all the other volatile oils subjected to analysis.

Volatile oils are applied to a great number of uses: Some of them are employed in medicine: some of them, as oil of turpentine, are much used to dissolve resins, which are afterwards employed as varnishes. Not to mention their employment in painting and in perfumery.

Oil of turpen-

Oil of turpentine, on which I shall make a few observations as constituting one of the most important of the volatile oils, is obtained by the distillation of various kinds of turpentine. What remains after the distillation is common rosin, which is employed in considerable quantity in the manufacture of yellow soap.

Properties of.

Oil of turpentine is transparent and colourless like water, it has a strong and peculiar smell and a hot acrid taste. It begins to boil usually about 314°, but as the boiling goes on the boiling point rises at least as high as 350°. It is obvious from this that common oil of turpentine constitutes a mixture of various oils, differing from each other in their volatility. When passed through a red-hot porcelain tube it is decomposed, a great quantity of lamp black is deposited, and carburetted hydrogen gas, mixed with a little carbonic oxide, issues from the extremity of the tube.

According to Saussure, it absorbs in 4 months 20 times its volume of oxygen gas, and a quantity of carbonic acid gas equal to 16 times its volume may then be driven out. By exposure to the air it becomes brown and thick. It then is found to contain a good deal of resin, which may be separated by distilling off the oil. If we heat it with peroxide of lead, vapours of water are exhaled, the oil becomes brown and thick, and at last constitutes merely a compound of oxide of lead and resin of a greyish white colour.

Oil of turpentine does not dissolve well in alcohol unless it Action on alcohol. be free from water. 100 parts of alcohol of 0.84 sp. gravity. dissolve 131 parts of oil of turpentine at 628. If we agitate impure oil of turpentine with 18th of its weight of alcohol of 0.83 sp. gr. the spirit dissolves the resinous portion and may be afterwards separated. By repeating this process three times we deprive the oil of all its resin, but it retains a portion of the alcohol, which may be separated by water. By dissolving a little oil of turpentine in alcohol we give the spirit the property of burning with splendour.

It absorbs a great deal of muriatic acid gas, and forms by combining with it the artificial camphor discovered by Kind. It is acted on pretty strongly by sulphuric acid; and nitric acid, especially, if it be mixed with a quantity of sulphuric acid, sets it on fire. It always reddens litmus paper, and therefore con-From the observations of Lecanu and Sertains a little acid. bat this acid appears to be the succinic.

It dissolves by digestion about half its weight of sulphur, sulphur, forming a red coloured solution. It is a good solvent of iodine, and is capable also of dissolving a little phosphorus. It is an excellent solvent of resins, and constitutes in consequence the medium by which various varnishes are obtained.

It absorbs 7½ times its volume of ammoniacal gas, 5 times ammoniacal its volume of cyanogen gas. Sulphurous acid gas and fluosilicic acid gas are also absorbed by it in considerable quantity. a medicine, oil of turpentine possesses considerable value. action depends upon the dose. When given in doses of 1 or 2 drachms it acts on the urinary organs so powerfully as sometimes to occasion bloody urine. When given in ounce doses it stimulates the bowels, and scarcely produces any effect upon the urinary secretions. In obstinate cases of costiveness it acts with more certainty than any other medicine. For the tenia it is almost a specific, discharging it in all cases dead. As an external application in rheumatism it is a medicine not to be

Chap. 111. despised. The quack medicine called essence of mustard is merely a solution of camphor in oil of turpentine.

#### SECTION VII. -- OF FIXED OILS.

History,

The fixed oils, which are of such extensive utility in the arts, were known at a very remote period. They are mentioned in Genesis, and during the time of Abraham were even used in lamps.\* The olive was very early cultivated, and oil extracted from it, in Egypt. Cecrops brought it from Sais, a town in Lower Egypt, where it had been cultivated from time immemorial, and taught the Athenians to extract oil from it. In this manner the use of oil became known in Europe.† But the Greeks seem to have been ignorant of the method of procuring light by means of lamps till after the siege of Troy; at least Homer never mentions them, and constantly describes his heroes as lighted by torches of wood.

Character.

FIXED OILS are distinguished by the following characters:

- 1. Liquid, or easily become so when exposed to a gentle heat-
- 2. An unctuous feel.
- 3. Very combustible.
- 4. A mild taste.
- 5. Boiling point not under 600°.
- 6. Insoluble in water and nearly so in alcohol.
- 7. Leave a greasy stain upon paper.

Preparation.

These oils, which are also called expressed oils, are numerous and are obtained partly from animals and partly from vegetables, by simple expression. As instances, may be mentioned whale oil or train oil, obtained from the blubber of the whale and from cod; olive oil, obtained from the fruit of the olive; linseed oil and almond oil, obtained from linseed and almond kernels. Fixed oils may also be extracted from poppy-seeds, hemp-seeds, beech-mast, and many other vegetable substances.

It deserves attention, that the only part of vegetables in which fixed oils are found is the seeds of bicotyledonous plants.‡ In animals they are most usually deposited in the liver, though they are found also in the eggs of fowls.

All these oils differ from each other in several particulars, but they also possess many particulars in common.

Liquidity.

1. Fixed oil is usually a liquid with a certain degree of viscidity, adhering to the sides of the glass vessels in which it is contained, and forming streaks. It is never perfectly transpa-

Gen. xv. 17. † Herodot. lib. ii. 59 and 62. ‡ Fourcroy, vii. 319.

rent, having always a certain degree of colour; most usually sect. VIL it is yellowish or greenish. Its taste is sweet, or nearly insipid. When fresh it has little or no smell.

There exist also in the vegetable kingdom a considerable number of bodies, which, at the ordinary temperature of the

atmosphere are solid, and have hitherto been considered as fixed oils. Palm oil may be mentioned as an example, which has been subjected to a chemical examination by Dr. Bostock.\* The various substances used in India and Africa as substitutes for butter, and as unguents, may likewise be mentioned. Most of them are obtained from the seeds of trees; different species of the bassia, as the butyracea, longifolia, latifolia, obovata, yield this butyraceous matter. They have been described by Dr. Roxburgh.+ The shea or butter tree of Africa, described by Park, seems also to be a species of bassia. These substances, from the experiments of Dr. Bostock, appear to differ a little from the liquid fixed oils in their properties, and to approach the nature of wax. Thus they are sensibly soluble in alcohol and ether, and do not combine so readily with alkalies as the fixed oils.

2. All the fixed oils hitherto examined are lighter than Specific grawater: but they differ greatly from one another in specific gravity. The same difference is observable in different samples of the same oil. The following table contains the specific gravity of such oils as have been examined:

Oil of palm <sup>†</sup> .	•	•	0.968
Hazel-nuts‡	•	•	0.941
Poppies‡	•	•	0.939
Linseed§	•	•	0.932
Almonds‡		•	0.932
Walnuts‡	•	•	0.923 to 0.947
Beech-nut‡	•	•	0.923
Ben‡ .	•	•	0.917
Olives		•	0.913
Rape-seed	•	•	0.913
Cacao¶		•	0.892
Neat's-foot o	il**	•	0.8795

3. Fixed oil does not begin to evaporate till it be heated Boiling point. above the boiling point of water. As the heat increases, a pretty copious vapour may be seen rising from it; but the oil

<sup>\*</sup> Nicholson's Jour. xvi. 161.

<sup>†</sup> Ibid. xix, 372.

<sup>‡</sup> Fabroni, Crell's Annals, 1797, ii. 123.

<sup>§</sup> Shaw's Boyle, ii. 346.

<sup>|</sup> Ibid. ¶ Brisson. \*\* As prepared in Ireland for machinery.

Chap. III. does not begin to boil till it is heated nearly up to the temper-At that temperature it may be distilled over, ature of 600°.\* but it is always somewhat altered by the process. Some water and acetic acid seem to be formed, a little charcoal remains in the retort, and the oil obtained is lighter, more fluid, and has a stronger taste than before. Oil, thus distilled, was formerly distinguished by the name of philosophical oil. During the distillation a great quantity of heavy inflammable air is obtained.

Fixed oil when in the state of vapour, takes fire on the approach of an ignited body, and burns with a yellowish white It is upon this principle that candles and lamps burn. The tallow or oil is first converted into the state of vapour in the wick; it then takes fire, and supplies a sufficient quantity of heat to convert more oil into vapour; and this process goes on while any oil remains. The wick is necessary to present a sufficiently small quantity of oil at once for the heat to act upon. If the heat were sufficiently great to keep the whole oil at the temperature of 600°, no wick would be necessary, as is obvious from oil catching fire spontaneously when it has been raised to that temperature. When oil is burnt in this manner, either in the open air or in contact with oxygen gas, the only new products obtained are water and carbonic acid.

When exposed to the action of cold, fixed oils lose their fluidity, and are converted into ice, but the freezing point varies in different oils.

Action of oxygen on.

- 4. When fixed oils are exposed to the open air, or to oxygen gas, they undergo different changes according to the nature of the oil. All of them, as far as experiment has gone, have the property of absorbing oxygen, and by uniting with it they become more and more viscid, and terminate at last in a solid state, being apparently saturated with oxygen. Now there are some oils that retain their transparency after they have become solid; while others become opaque, and assume the appearance of tallow or wax. This circumstance has given occasion to the division of the fixed oils into two classes: Those that remain transparent are called drying oils, while those that become opaque are called fut oils. To these two we may add a third class, namely, those that are presented by nature in a solid state, which we shall call solid oils. Let us take a view of these three classes of fat oils in succession.
- \* Linseed oil, according to Morveau, boils at 590°. Ann. de Chim. xc. 122. Whale oil boils at 640°, and may be heated up to 650°. After being distilled over it boils at 410%.

Sect. VII.

# I. Drying Oils.

The principal drying oils are the following:

List of drying

- 1. Linseed oil, from the seeds of linum usitatissimum.
- 2. Walnut oil, from the seeds of juglans regia.
- 3. Hemp oil, from the seeds of cannabis sativa.
- 4. Poppy oil, from the seeds of papaver somniferum.
- 5. Castor oil, from the seeds of ricinus communis.
- 6. Croton oil, from the seeds of croton tiglium.
- 7. Grape-seed oil, from the seeds of vitis vinifera.
- 8. Nightshade oil, from the seeds of atropa belladonna.
- 9. Tobacco oil, from the seeds of nicotiana tabacum.
- 10. Henbane oil, from the seeds of hyoscyamus niger.
- 11. Sunflower oil, from the seeds of helianthus annuus.
- 12. Cress oil, from the seeds of lepidium sativum.

Doubtless drying oils may be obtained likewise from various other plants.

These oils, in their natural state, possess the property of How predrying oils but imperfectly. To prepare them for the use of the painter and varnish-maker they are boiled for some time in an iron pot. By this process they are partly decomposed; abundance of watery vapour and of carburetted hydrogen gas is separated from them. They become deeper coloured, and acquire greater consistency. It is common for some purposes to set them on fire, to allow them to burn for some time, to extinguish them by covering up the vessel in which they are contained, and to continue the boiling till they acquire the proper degree of viscidity. By this process they lose their unctuous quality in a great measure, so as not to leave a greasy stain upon paper, and approach the nature of resins, with this difference, that they do not become brittle, but retain a degree of toughness and ductility not unlike what in this country is called wrought rosin, or shoemakers' rosin. It is common also in preparing the drying oils to boil them with a little litharge. The change which happens to the oils by this process has not been precisely ascertained. Probably they absorb oxygen from the air, and we know that they undergo a partial decomposition. When they burn for some time, their unctuous quality is much more completely destroyed than by any method which has yet been practised. Hence it is followed frequently in preparing the drying oils for varnishes, and always for printers' ink, which requires to be as free as possible from all unctuosity.

Nut oil has been found preferable to all other oils for printers'

Chap. HL ink; though the dark colour which it acquires during boiling renders it not so proper for red ink as for black. Linseed oil is considered as next after nut oil in this respect. Other oils cannot be employed, because they cannot be sufficiently freed from their unctuosity. Ink made with them would be apt to come off and smear the paper while in the hands of the bookbinder, or even to spread beyond the mark of the types, and stain the paper yellow. The process for making printers' ink is as follows:

Printers' ink.

The oil is made to boil in an iron pot only half filled, set on ofire, and allowed to burn for half an hour or more, then boiled gently till it acquires the proper consistence. In this state it is called the varnish. Two kinds are prepared, a thicker and The thicker is of such a consistence that it draws a thinner. into threads when cold like weak glue. This varnish is afterwards ground with lamp-black in the proportion of two ounces and a half to sixteen ounces of oil. When newly prepared oil is used for making ink, it is said to be necessary to add a little boiled oil of turpentine and a little litharge; but this is said to have the effect of causing the ink to stick so firmly to the types, that it can with difficulty be removed. Old oil does not require this addition.\*

Oil prepared by the process above described, is still insoluble in alcohol and water, but it unites readily to more oil. into a tough mass like turpentine, and afterwards is scarcely susceptible of uniting with oil. Dr. Lewis found that linseed oil, when thus converted into a thick varnish, lost 1th of its weight; when boiled till it became quite stiff when cold, it lost nearly one-half of its weight.+ The property which printers' ink has of adhering to moistened paper shows that the oily nature of the body is greatly altered. In some respects it has approached the nature of mucilage, though in others the difference is very great.

### II. Fat Oils.

List of fat

The principal fat oils are the following:

- 1. Olive oil, from the fruit of the Olea Europæa.
- 2. Almond oil from the amygdalus communis.
- 3. Rape oil, from the brassica rapa.
- 4. Mustard oil, from sinapis alba and nigra.
- 5. Plumb oil, from prunus domestica.

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- 6. Beech oil, from fagus sylvatica.
- 7. Hazel oil, from corylus avellana.
- 8. Oil of ants.
- 9. Oil of eggs.
- 10. Trane or whale oil.
- 11. Spermaceti oil.

When oil is poured upon water, so as to form a thin layer on its surface, and is in that manner exposed to the atmosphere, these changes are produced much sooner. Berthollet, who first examined these phenomena with attention, ascribed them to the action of light; but Sennebier observed that no such change was produced on the oil though ever so long exposed to the light, provided atmospherical air was excluded; but that it took place on the admission of oxygen gas, whether the oil was exposed to the light or not.\* It cannot be doubted then, that it is owing to the action of oxygen. It is supposed at present to be the consequence of the simple absorption of oxygen and its combination with the fat oils.

### III. Solid Oils

The principal solid oils are the following:

List of solid

- Cacao butter, from theobroma cacao.
   Palm oil, from cocos butyracea.
- 3. Muscat balsam, from myristica officinalis.
- 4. Laurel oil, from laurus nobilis.
- 5. Japan wax.
- 6. Myrtle wax, from myrica cerifera.
- 7. Bees' wax.
- 8. Coco oil, from cocos nucifera.
- 9. Butter of galam.
- 10. Hog's lard.
- 11. Common butter.
- 12. Tallow.

These solid bodies differ from each other very much in the temperature at which they become liquid. Palm oil, which is used in this country to give common soap a yellow colour, melts at 84°; japan wax melts at about 98°.

We are indebted to the investigations of Chevreul for a great deal of important information respecting the fixed oils. He ascertained that they are all compounds consisting of two or three different substances, which may be separated by

chan III. processes which he pointed out. These substances he has distinguished by the names of stearine, elaine, cetine, phocenine, butyrine, hircine, and cholesterine. Let us take a view of these seven substances, which may be considered as the first principles or constituents of oily bodies in general.

#### 1. Stearine.

History.

This substance was first described by Chevreul in 1814.\*
It was pointed out likewise by Braconnot in 1815, who did not seem aware of what had been previously done by Chevreul;
or at least took no notice of it.+

It appears from the experiments of Chevreul that tallow and animal fat of every kind is a mixture or combination of two distinct oily substances. The first of these, which is solid at the usual temperature of the air, he has called *stearine*;‡ to the second, which is liquid at the same temperature, he has given the name of *elaine*.§ From the experiments of Braconnot it would appear that the fixed oils of the vegetable kingdom have the same composition.

Preparation.

Chevreul obtained stearine from hog's lard by the following process. The lard, purified as completely as possible from foreign matter, was heated in boiling alcohol. When the alcohol cooled it deposited white crystalline needles, which were stearine. This process was repeated till the whole of the lard was dissolved in the alcohol. The stearine thus obtained in crystals was dissolved a second time in alcohol, and allowed to separate in crystals. By this process the whole of the elaine is not separated from the stearine; though probably the quantity which remains is not considerable.

The method employed by Braconnot was very simple, and seems to show that in fixed oily bodies the stearine and elaine are not in chemical combination; but merely mechanically mixed with each other. If the oil to be examined was liquid,

Alcohol of the sp. gr. 0.7925 dissolved  $\frac{16.0}{1100}$ . Alcohol of the sp. gr. 0.805 dissolved  $\frac{6.65}{100}$ . Alcohol of the sp. gr. 0.821 dissolved  $\frac{200}{100}$ .

Ann. de Chim. et Phys. H. 361.

<sup>\*</sup> Ann. de Chim. xciv. 129. See also Ann. de Chim. xciv. 74, and Chevreul sur les corps gras, p. 178.

<sup>†</sup> Ann. de Chim. xciii. 225. ‡ From στιας, tallow. § From ελαιον, oil. ¶ The process is greatly facilitated by using absolute alcohol. For the solubility of stearine, in alcohol, diminishes at a much greater rate than the strength of that liquid. Chevreul found that boiling alcohol of the sp. gr. 17908 dissolved more than its weight of stearine.

he exposed it to cold till it congealed. In this congealed state it was subjected to strong pressure between folds of blotting paper. The elaine was imbibed by the paper, and the stearine remained behind in a solid state. If the oil to be examined was already solid, it was not necessary to expose it to cold. It was simply subjected to pressure between folds of blotting paper.

Stearine obtained by these processes is white, brittle, and has properties somewhat the appearance of wax. It has little or no smell when pure. It is tasteless, and produces no change on vegetable blues. Stearine from hog's lard becomes liquid when heated to the temperature of 109°. But there is a considerable difference in the melting point of the stearine from different bodies. This will appear by the following table.\*

Stearine	from	humar	ı tallo	w fus	es at	•	•	120°
	,	sheep	•		•	•	•	109
		oxen				•	•	111
		hog	•			•	•	109
		duck	_	_	_	_	_	109

It is soluble in alcohol, but the stearine from different bodies varies somewhat in its solubility. This will appear by the following table, for the experiments contained in which we are likewise indebted to Chevreul. 100 parts of boiling alcohol of the specific gravity 0.7952, dissolve

21.50 of stearine from man, 16.07 of stearine from the sheep, 15.48 of stearine from the ox, 18.25 of stearine from the sow, 36.00 of stearine from the duck.

When stearine is digested with an alkaline substance the greatest part of it is converted into soap, only a small portion of it becomes the sweet principle of oils, and a still smaller is acetic acid. The following table, likewise drawn up by M. Chevreul, gives the proportion of stearine from different bodies turned into soap by the action of potash, and the proportion that continued soluble:

Stearine of man			C Portion saponified		94.9
Stearme of man	•	•	? Portion soluble .	•	5.1

100.0

2 A

II.

<sup>\*</sup> Chevreul; Ann. de Chim. et Phys. ii. 363.

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Stearine of the sheep			<b>Saponified</b>	•	•	94.6
Stearine of the sneep	•	•	Soluble .	•	•	5.4
						100.0
Stearine of the ox.			Saponified	•	•	95·1
Stearine of the ox.	•	•	{ Soluble .	•	•	4.9
						100.0
C C.1 1			<b>Saponified</b>			
Stearine of the hog	•	•	Soluble .	•	•	5.35
						100.00
C( ! C(1 - 1 - 1			( Saponified	•		
Stearine of the duck	•	•	{ Soluble .	•	•	<b>5·6</b>
						100.0

Stearine usually crystallizes in small needles, and when a quantity of it is melted and allowed to congeal, the surface becomes very uneven.

Stearine from man, when saponified, is converted into margaric acid alone, while stearine from the sheep yields both margaric and stearic acids.

Composition.

The constituents of stearine from sheep, as determined by Chevreul, are

Oxygen	•	•	•	9.454
Carbon	•	•	•	78.776
Hydrogen		•	•	11.770
				100.000

This is equivalent to

atoms oxygen,22.228 atoms carbon,19.92 atoms hydrogen.

If we adopt

1 atom oxygen, 11 atoms carbon, 10 atoms hydrogen,

it is evident that it might resolve itself into

1 atom carbonic oxide,

1 atom of a carbo-hydrogen, composed of 10 atoms carbon and 10 atoms hydrogen.

Elaine may be obtained from the tallow of different animals Preparation. by Chevreul's process. He dissolves the tallow in alcohol, allows the stearine to crystallize, and then distils off the alcohol from the elaine. Braconnot's method appears of easier execution, and will probably yield elaine of greater purity. He procures his stearine by subjecting the tallow to pressure between folds of blotting paper. The paper imbibes the elaine. To separate it he soaks the paper in water, and subjects it to pressure, the elaine is forced out, and may easily be collected and examined.

It has very much the appearance of a vegetable oil, and is Properties, quite liquid at the temperature of 59°. Sometimes it is colourless and destitute of smell; but most commonly it has both, owing to the presence of foreign bodies from which it is not possible to free it. Chevreul examined particularly elaine from the tallow of man, the sheep, the ox, the hog, the jaguar, and the goose. The following are the properties of each:

- 1. Elaine of man—yellow, without smell, of the sp. gravity 0.913.
- 2. Elaine of the sheep—colourless, a slight smell of mutton, sp. gravity 0.916.
- 3. Elaine of the ox—colourless, almost without smell, sp. gravity 0.913.
- 4. Elaine of the hog—colourless, almost without smell, sp. gravity 0.915.
- 5. Elaine of the jaguar—lemon yellow, having an odour, sp. gravity 0.914.
- 6. Elaine of the goose—slightly yellow, almost without smell, sp. gravity 0.929.

The solubility of these different varieties of elaine in alcohol of the sp. gravity 0.7952 was as follows:

- 1. Elaine of man—100 parts dissolved in 81.08 parts of boiling alcohol, the solution began to become opaque at 170°.
- 2. Elaine of the sheep—100 parts were dissolved by 81·17 of alcohol at the temperature of 167°, the liquid became muddy at 145°.
- 3. Elaine of the ox—100 parts were dissolved by 81.03 of alcohol at the temperature of 167°, the liquid became muddy at 145°.
  - 4. Elaine of the hog-100 parts were dissolved by 81.08 of

alcohol at the temperature of 167°, the liquid became muddy at 143°.

- 5. Elaine of the jaguar—100 parts were dissolved by 80.89 of alcohol at the temperature 167°, the liquid became muddy at 140°.
- 6. Elaine of the goose—100 parts were dissolved by 81.08 of alcohol of the temperature 167°, the liquid became muddy when cooled down to 124°.

When these different varieties of elaine were digested for a sufficient time with potash lye, by far the greatest part was converted into soap. But the soluble portion, consisting chiefly of the sweet principle of oils, was rather greater than the quantity formed when stearine was saponified in the same way. The following table exhibits the proportions of elaine saponified and converted into sweet principle, when the experiment was made with the different varieties above specified.

1. Elaine from the sheep, hog, jaguar, and goose.

	Saponified	_ •		•	_		89
	Soluble	•				•	11
							100
2. Elaine	of the ox.						
	Saponified	•			•		92.6
	Soluble	•	•		•		7.4
							300.0*
							100.0*

To give the reader an idea of the proportion of stearine and elaine in different varieties of fixed oil, animal and vegetable, I shall insert the following table exhibiting the proportions of each, which Braconnot obtained by his experiments:

Butter		Stearine	•	•	40
Dutter	•	<b>Elaine</b>	•	•	60
Hogslard .		<b>Stearine</b>	•	•	38
Hogsiard .	•	<b>Elaine</b>		•	<b>62</b>
Beef marrow .	•	ς Stearine	•	•	<b>76</b>
Deel marrow .	• 1	{ Elaine	•	•	24
Mutton marrow		<b>Stearine</b>	•	•	<b>26</b>
Mutton mariow	•	<b>Elaine</b>	•	•	74
Goose fat .		<b>ς</b> Stearine	•	•	<b>32</b>
Goose lat .	•	Elaine		•	68

<sup>\*</sup> Chevreul; Ann. de Chim. et Phys. ii. 366.

<sup>†</sup> Ann. de Chim. xciii. 225.

D 1.C.			Stearine Elaine	•	•	<b>2</b> 8	Sect. VII.
Duck fat	•	•					
77l			Stearine Elaine	•	•	<b>26</b>	
Turkey fat	•	٠.	<b>Elaine</b>	•	•	74	
Olive oil			Stearine Elaine	•	• `	28	
Onve on	•	•	<b>Elaine</b>	•	•	<b>72</b>	
Almond oil		•	Stearine Elaine	•	•	24	
Aimond on	•	•	<b>Elaine</b>	•	•	<b>76</b>	
Oil of colsa			ς Stearine	•	•	<b>46</b>	
On or coisa	•	•	¿ Elaine	•	•	<b>54</b>	

The constituents of claime, as determined by Chevreul, are as follows:

Oxygen	•	•	9.987	Composition.
Carbon .	•		<b>78·566</b>	
Hydrogen	•	•	11.447	
			100.000	

These numbers are equivalent to

1 atom oxygen, 10.48 atoms carbon, 9.17 atoms hydrogen.

Were we to adopt

1 atom oxygen, 10 atoms carbon, 9 atoms hydrogen,

as the true constitution, then we might consider it as a compound of

1 atom carbonic oxide,

1 atom of a carbo-hydrogen, composed of 9 atoms carbon and 9 atoms hydrogen.

This would reduce the difference between stearine and elaine to one atom less carbon and hydrogen in the carbo-hydrogen, of which the latter is chiefly composed.

### 3. Cetine.

The spermaceti of commerce, from which cetine was extracted by Chevreul, always contains a yellow oil, from which it was freed in the following manner:

50 parts of spermacetifusible at 111° were triturated in 50 Preparation. parts of cold alcohol of the specific gravity 0.816, and the mixture was left for 24 hours at a temperature of about 68° and then filtered. The undissolved residue was treated with 100 parts of boiling alcohol in a flask, and the whole allowed to

Chap. III. cool. The crystals and the undissolved portion were treated with successive portions of boiling alcohol till the alcohol when evaporated ceased to exhibit any traces of oil. The residual matter was considered as pure cetine. It melted at the temperature of 120°.

Properties,

On cooling it crystallizes in white brilliant plates. temperature of about 680° it may be volatilized without decomposition. It has a very slight smell, but is destitute of taste. It is insoluble in water. 100 parts of alcohol of the specific gravity 0.821 dissolve 2.5 parts of cetine, the greatest part of •which is deposited as the solution cools in crystalline plates having a pearly lustre. Cetine produces no change on vegetable blues.

Potash converts it into ethal and margaric and oleic acids. When heated sufficiently in an open dish it takes fire and burns Sulphuric acid gradually decomposes it when assisted The action of nitric acid on it is similar to the action by heat. of the same acid on stearic acid. The constituents of cetine, as determined by Chevreul, are as follows:

Composition.

Öxygen	•	•	5.478
Carbon	•	•	81.660
Hydrogen	•	•	12.862

100.000\*

These numbers give us the atomic constitution of cetine as follows:

> atom oxygen, 19.8 atoms carbon. 18.75 atoms hydrogen.

Perhaps we may adopt the following atoms as coming sufficiently near the result of the analysis,

> l atom oxygen, 20 atoms carbon, 19 atoms hydrogen.

This would make cetine a compound of

1 atom carbonic oxide,

1 atom carbo-hydrogen, composed of 19 atoms carbon and 19 atoms hydrogen.

Or if we consider the carbo-hydrogen as the same as exists in elaine, then cetine contains only half the oxygen that exists in elaine.

<sup>\*</sup> Sur les corps gras, p. 170.

This substance was extracted by Chevreul from the oil of the delphinus phocæna or common *porpoise*, in the following manner:

200 parts of porpoise oil were mixed with 180 parts of alco-preparation. hol of the specific gravity 0.797 and slightly heated, the whole was dissolved. After 24 hours the alcohol which swam on the surface of the oil was decanted off and distilled. There remained an acid oil of the specific gravity 0.931 at the temperature of 61°. It was deprived of its acid portion, and then treated withoweak cold alcohol. By this means phocenine was obtained.

It is a very fluid oil, having a specific gravity of 0.954. Its Properties. odour is slight, but peculiar, and having some resemblance to that of phocenic acid. It does not act upon vegetable colours. Alcohol dissolves it in great abundance when assisted by heat. When a dilute alcoholic solution is distilled, the phocenine remaining has acid properties; but the quantity of acid formed is very small. When 100 parts of phocenine are treated with potash, they are converted into

			106.82+
Glycerine*	•	•	15.00
Oleic acid, hydrous	•	•	<b>59·00</b>
Pure phocenic acid	•	•	32.82

## 5. Butyrine.

Chevreul found, on examining butter, that it contained two distinct oily bodies; besides a solid constituting a variety of stearine. One of these oils possessing peculiar properties, he gave it the name of butyrine. He obtained butyrine by the following process:

The butter was first freed from all traces of buttermilk. It preparation was then cooled very slowly in a deep porcelain dish, and kept for some days at a temperature of 66°. By degrees it separated into a granular substance, consisting of stearine, still retaining a certain portion of the two oils of butter, and a liquid consisting of the two oils, still retaining in solution a portion of stearine. This liquid portion being filtered was found to possess the following properties: Its colour was yellow, and its taste and smell similar to that of butter. At 66° its specific gravity was

<sup>\*</sup> By this is meant the sweet principle of oils discovered by Scheele.

<sup>†</sup> Chevreul, sur les corps gras, p. 190.

of alcohol of 0.821 dissolved 6 parts of it when assisted by a boiling heat.

88 parts of this liquid oil were mixed in a flask with 88 parts of alcohol of the specific gravity 0.796. The mixture was agitated and left to digest for 24 hours in the temperature of 66°. The alcohol was drawn off after 24 hours, and replaced by 176 parts of new alcohol, which was drawn off in its turn after 24 hours, and 176 parts of new alcohol substituted. This last portion dissolved the whole, but when the alcohol was allowed to cool, a portion of oil precipitated. The alcohol was separated from the solution by a cautious distillation. The residual oil contained a little acid, which was removed by digestion with magnesia, and then washing with water. Thus purified it was butyrine in a state of purity.

Properties.

Butyrine thus obtained is very fluid at 66°, and has a specific gravity of 0.908. It is usually yellow, but this colour is not essential to it, as some butters give a butyrine quite white. It has a smell similar to that of butter. It does not congeal when cooled down to 32°. It has no action on vegetable colours. It is insoluble in water, but alcohol of the specific gravity 0.822 dissolves it in any proportion whatever, at a boiling temperature. A solution of 20 parts of butyrine in 100 alcohol becomes opaque on cooling; but 120 parts of butyrine in 100 of alcohol remains transparent. When the alcoholic solution is distilled the butyrine becomes acid, a small quantity of butyric acid being developed. It is readily saponified, and by the process is converted into butyric acid, margaric acid, and oleic acid; together with about 12.5 per cent. of glycerine.

### 6. Hircine.

Hircine is a liquid oil, which exists in the tallow of the deer and the sheep. It is it which forms with elaine, the liquid portion of tallow. It is characterized by yielding hircic acid when saponified.\*

#### 7. Chôlesterine.

Preparation.

This name has been given by Chevreul to a fatty matter like spermaceti, which constitutes the principal constituent of biliary calculi, and which Fourcroy had distinguished by the name of adipocire. Cholesterine may be obtained by washing human

<sup>\*</sup> Chevreul, sur les corps gras, pp. 151, 195.

biliary calculi with water, and then dissolving them in boiling Sect. VII. hot alcohol. As the solution cools the cholesterine is deposited in crystalline plates. When these are washed in alcohol, and dried, they constitute pure cholesterine.

It is solid, white, and possessed of considerable lustre. It Properties. melts when heated to 278°. When allowed to cool slowly, after being brought into a state of fusion, it crystallizes in radiating plates. It has no taste, and is almost destitute of smell. At 680° it may be volatilized without undergoing decomposition.

It is insoluble in water. . 100 parts of boiling alcohol of the specific gravity 0.816, dissolve 18 parts of cholesterine. But if the specific gravity of the alcohol be 0.840, it will dissolve only 11.24 of this substance. The alcoholic solutions on cooling, deposite most of the cholesterine in crystals. It has no action on vegetable blues. It gives out no water when heated with protoxide of lead. It cannot be converted into a soap, nor does it undergo any alteration when digested with potash ley. When heated sufficiently in an open dish it burns like wax. Sulphuric acid decomposes it when assisted by heat. It is also decomposed by hot nitric acid. Its constituents, as determined by the analysis of Chevreul, are as follows:

> Oxygen Carbon 85.095 Hydrogen 11.880

Composition,

100.000\*

This is equivalent to the following atomic quantities:

l atom oxygen,

35.8 atoms carbon,

31.4 atoms hydrogen.

If we admit the atomic constitution to be

l atom oxygen,

36 atoms carbon,

31 atoms hydrogen.

it is obvious that it cannot, like the preceding bodies, be resolved into carbonic oxide and carbo-hydrogen. But it might be resolved into

- 1 atom carbonic oxide,
- 1 atom carbo-hydrogen, consisting of 27 atoms carbon and 27 atoms hydrogen,
- 1 atom super-carburetted-hydrogen, consisting of 8 atoms carbon, and 4 atoms hydrogen.

<sup>\*</sup> Chevreul, sur les corps gras, p. 153.

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An elaborate set of experiments has been made by M. de Saussure, to determine the elementary constitution of several of the fixed oils; but no very important conclusions could be drawn from such analyses, unless the different substances, of which almost all these bodies are composed, had been previously insulated, and analyzed separately. The following table exhibits the results of Saussure's analyses. I have introduced likewise a few other analyses of fixed oils made by other chemists.

Constituents of fixed oils.

}	Carbon,	Hydrogen.	. Oxygen.	Azote.	Total.	Experimenters.
Linseed oil	76.014	11.351	12.635	0	100	Saussure.
Nut oil	79.774	10.570	9.122	0.534	100	Ditto.
Almond oil	77.403	11.481	10.828	0.288	100	Ditto.
Castor oil	74.178	11.034	14.788	0	100	Ditto.
Olive oil	76.034	11.545	12.068	0.353	100	Ditto.
Hog's lard	74.792	11.652	13.556	0	100	Ditto.
Train oil	76.1	12.4	11.5	0	100	Berard.
Spermaceti oil	78.91	10.97	10.12	0	100	Ure.
Oil of ants		15.06	4.05	19.59	100	Göbel.
Butter	65.6	17.6	16.8	0	100	Berard.
Bees wax	81.607	13.359	4.534	0	100	Saussure.
Spermaceti	75.474	12.795	11.377	0.354	100	Ditto.
Rosin	77.402	9.551	13.047	0	100	Ditto.
Cholestine	84.068	12.018	3.914	0	100	Ditto.
Elaine of hogslard	74.792	11.652	13.556	0	100	Ditto.
Stearine of Stearine of	82·170	11.232	6.302	0.296	100	Ditto.

When the fixed oils are saponified they are converted into the various fatty acids described in the first chapter of this volume, and into glycerine. Chevreul considers it as probable that they are compounds of glycerine and these acid bodies, having in this respect some resemblance to the acid ethers. The alkalies, by combining with the acid, set the glycerine at liberty. It would not be easy to verify this conjecture by experiment. Our mode of purifying the different constituents of the fixed oils, such as they have been described in this section, and obtaining each in a separate state, is too imperfect to warrant much confidence in the accuracy of the analyses that have been made, or to enable us to deduce from them conclusions of much importance.

The fixed oils are all insoluble in water. When agitated Sect. VII. with that liquid, the mixture becomes milky, but the oily par- Properties, ticles gradually separate and swim upon the surface. presence of a mucilaginous substance, as gum arabic, prevents the oil from separating, and occasions, of course, a permanent Such mixtures are called emulsions. They are often formed by triturating oily seeds, as almonds, with water; the two ingredients necessary to form an emulsion, oil and mucilage, being present in the seed.

Most of the fixed oils are but sparingly soluble in alcohol. Mr. Brande found that very little olive or almond oil was taken up by alcohol of the specific gravity 0.820. Linseed oil is more soluble, and alcohol dissolves any quantity whatever of castor oil. On that account this oil is sometimes employed to adulterate volatile oils of high value, especially oil of cloves.\*

In general the fixed oils are somewhat more soluble in sulphuric ether than in alcohol. Four measures of sulphuric ether of the specific gravity 0.7563 were found by Mr. Brande to dissolve  $1\frac{1}{4}$  measure of almond oil,  $1\frac{1}{6}$  measure of olive oil,  $2\frac{1}{6}$ measures of linseed oil, and any quantity whatever of castor oil.+

The fixed oils unite readily with each other, with volatile oils, and likewise with bituminous and resinous substances.

The alkalies unite readily with the fixed oils, and form the important compounds called soaps. The fat oils enter into these combinations more readily than the drying oils. The earths likewise combine with these oily bodies, and form a kind of soap insoluble in water, and are therefore not capable of being applied to the same uses as common soap.

The combustible acids, as far as is known at present, do not unite with oils; neither has the muriatic acid any remarkable effect. Phosphoric acid, when concentrated, deepens their colour, and gives them a peculiar smell, especially if assisted by heat: a proof that it acts upon them. † The sulphuric acid acts with much greater energy. The oils become immediately black, and assume gradually the properties of bitumen in proportion to the continuance of the action. If the acid be allowed to remain long enough, they are completely decomposed; water is formed, charcoal precipitated, and an acid evolved.§ Other

<sup>\*</sup> Phil. Trans. 1811, p. 264.

<sup>+</sup> Ibid. Equal volumes of sulphuric ether and castor oil united together has been found a useful external application in rheumatism.

<sup>‡</sup> Elemens de Chimie of the Dijon Academy, iii. 142.

<sup>§</sup> Fourcroy, vii. 330.

Chap. III. products doubtless also make their appearance, though the action of this acid on oils has not yet been examined with sufficient care. Nitric acid acts with still greater energy. When poured suddenly upon the drying oils, it sets them on fire. The same effect is produced upon the fat oils, provided the acid be mixed previously with a portion of the sulphuric. When the nitric acid is sufficiently diluted, it converts the drying oils into a yellow resinous-like mass, and the fat oils to a substance very But the action of this acid upon fixed oils has not like tallow. yet been sufficiently examined.

> Many attempts have been made by chemists to form permanent compounds of the concentrated acids and oils, under the name of acid soaps. The only acid which was found to answer was the sulphuric. Achard published a number of experiments on these compounds. They dissolve in water, and lather like common soap; but as they are not in reality permanent compounds, they cannot be used with much prospect of advantage.

> The fixed oils acts (though feebly) upon some of the metals when the atmospheric air is not excluded. Copper is soon corroded by them, and a dark green solution obtained. only other metal upon which they are known to act in the same manner is mercury. By triturating mercury with fixed oils, it gradually disappears, and a bluish coloured unguent is formed; consisting, in part at least, of the black oxide of that metal united to the oil. But this experiment scarcely succeeds, except with those oils which are in a state approaching to solidity.

> But upon the metallic oxides the fixed oils act with greater energy. They dissolve the white oxide of arsenic with great facility, as was shown long ago by Brandt. When boiled with the oxides of mercury, lead, or bismuth, they form very tough solid compounds, called plasters.

> Fixed oils are liable, by keeping, to undergo a change well known by the name of rancidity. They become thick, acquire a brown colour, an acrid taste, and a disagreeable smell. oil thus altered converts vegetable blues into red, and of course contains an acid. It is believed at present that this change is owing to the alteration of the foreign substances present in oils, or to the action of those foreign bodies upon the oily matter Several of the fixed oils, when newly extracted, let fall on standing a quantity of mucilaginous matter; and from the experiments of Scheele, it appears probable that they always retain less or more of a similar principle. He boiled together one part of litharge, two parts of olive oil, and a little water.

When the oil had acquired the consistence of an ointment, it seek VIII. was allowed to cool, and the water decanted off. When this water is evaporated to the consistence of a syrup, it leaves a substance which Scheele termed the sweet principle of oils. does not crystallize, is soluble in water and alcohol, and is converted into oxalic acid by the action of nitric acid. When heated, it is partly decomposed into a brown oil, and partly volatilized unaltered. This substance he obtained also from linseed and rape-seed oil, and from oil of almonds. Even the oil disengaged from soap yielded him a little of it.\* impurities were supposed to exist in all fixed oils, and to occasion their rancidity by putrefaction. This rancidity is in some degree diminished by agitation with water, but not completely destroyed. Mr. Dossie has shown that agitation with the fixed alkaline solutions and quicklime answers the purpose sufficiently well in purifying oils for burning in lamps; but that they have the property of coagulating a portion of the oil. This however may be prevented by adding a quantity of strong brine, which occasions the separation of the foreign bodies from the oil.

#### SECTION VIII .-- OF BITUMENS.

The term bitumen has often been applied by chemists to all the inflammable substances that occur in the earth; but this use of the word is now so far limited, that sulphur and mellite are most commonly excluded. It would be proper to exclude amber likewise, and to apply the term to those fossil bodies only which have a certain resemblance to oily and resinous substances. In this restricted sense the word is used in the present section.

Bituminous substances may be subdivided into two classes: namely, bituminous oils and bitumens, properly so called. first set possess nearly the properties of volatile oils, and ought in strict propriety to be classed with these bodies; but as the chemical properties of bitumens have not yet been investigated with much precision, it was deemed rather premature to separate them from each other. The second set possess properties peculiar to themselves. Let us endeavour to describe the substances belonging to these two classes as far as possible.

### 1. Bituminous Oils.

Only two species of bituminous oils have been hitherto examined by chemists. Others indeed have been mentioned, but

Chap. III. their existence has not been sufficiently authenticated. These two species are called petroleum, and maltha, or sea-wax; the first is liquid, the second solid.

1. Petroleum is an oil of a brownish yellow colour. pure, it is as fluid as water, and very volatile.\* Its specific gravity varies from 0.730 to 0.878.† It has a peculiar smell. When heated, it may be distilled over without alteration.

How ob. tained.

Petroleum is found in the earth in various states of purity; sometimes without any mixture of foreign substances. In this state it is usually distinguished by the name of naphtha, and is said to occur in great abundance on the shores of the Caspian and in Persia. It occurs also in different parts of Europe, especially Italy and Germany. When less fluid and darker coloured, it is commonly called petroleum. It is supposed to owe this increased spissitude and deepened colour to the action of the air. When distilled, it yields a quantity of pure petroleum, while a portion of bitumen of the consistence of tar or pitch When long exposed to the air, petroleum remains behind. becomes black, and acquires the semifluidity of tar. In this state the greatest part of it is insoluble in alcohol; so that it has assumed the state of true bitumen.

Petroleum is used in those countries, where it abounds, as an oil for lamps. It is employed also as a solvent of resinous bodies, and of the proper bitumens, which it dissolves with facility.

Naphtha.

When petroleum is distilled at a low heat, the liquid which comes first over is distinguished by the name of naphtha. is colourless, perfectly fluid; is very volatile, and has a peculiar smell. Coal tar, or the oily matter which comes over when coal is distilled at a red heat, yields, when repeatedly rectified, the very same kind of liquid. Naphtha is observed also in different places rising spontaneously from the earth nearly in a state of purity. As, for example, in different parts of Persia, at Amiano in Italy, and in many other places. This natural production of naphtha is observed in many places where no coal has been ever discovered. Yet I think it not improbable, from the exact similarity between the properties of natural naphtha and coal naphtha, that they have in reality the same origin.

<sup>\*</sup> The volatility seems to have been over-rated by older chemical writers. On mixing well rectified petroleum with water in a retort, I found that the water could be readily distilled over in a moderate heat, while the whole petroleum remained behind.

<sup>+</sup> See Kirwan's Mineralogy, ii. 42.

The specific gravity of naphtha varies considerably, probably according to its state of purity. The following are the specific gravities which I have myself ascertained.

1. Persian naphtha, not rectified . . 0.753

2. Coal naphtha, perfectly colourless . . 0.817\*

3. Coal naphtha, slightly yellow . 0.850+

4. Natural naphtha of Amiano . . . 0.836‡

5. Ditto, thrice rectified · . . . 0.758‡

Naphtha is very volatile: a drop of it let fall on paper disappears in a few minutes. Yet its boiling point is rather higher than that of oil of turpentine. I found that Persian naphtha began to boil in glass at the temperature of 320°. As the boiling continues the temperature rises. I raised the temperature of Persian naphtha in a silver cup as high as 352°.

At the temperature of 72.5° the vapour of naphtha is capable of supporting a column of mercury 1.78 inch in height. M. T. de Saussure determined its specific gravity by weighing a mixture of vapour of naphtha and common air. He obtained 2.833 as the specific gravity. I tried the specific gravity of the vapour of Persian naphtha at the temperature of 55° by the same method, and found it 2.263. Saussure's experiment was made at the temperature of 72.5°. Probably, therefore, the specific gravity of this vapour increases at a great rate with the temperature. When the vapour of naphtha is mixed with common air, it is not easily removed again. It may be passed, without alteration, through water. Alcohol would no doubt absorb it, and a considerable proportion of it would be condensed by the freezing temperature.

Naphtha burns with a strong yellow flame, and a considerable smoke.

It is insoluble in water; though it communicates its peculiar Properties. smell to that liquid. Alcohol dissolves about \( \frac{1}{3} \)th of its weight of it. Sulphuric ether, petroleum, fat oils, pitch, volatile oil, combine with naphtha in every proportion. It dissolves wax by the assistance of heat, and allows a portion of it to fall down again as it cools. Caoutchouc swells in naphtha to more than 30 times its bulk, and becomes gelatinous and transparent; but scarcely dissolves. However, by this means it is easy to mould caoutchouc into tubes of considerable service to the chemist.\( \)

<sup>\*</sup> It had been manufactured in Edinburgh.

<sup>+</sup> It had been manufactured in Glasgow.

<sup>1</sup> Determined by Saussure, Annals of Philosophy, x. 119.

<sup>§</sup> See Mr. Syme's paper, Annals of Philosophy, xii. 112.

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Naphtha dissolves a little sulphur and phosphorus when assisted by heat, and lets them fall again in the state of crystals. Neither the fixed alkalies nor the strong mineral acids have any marked action on naphtha. It is known that anhydrous potash combines with it and forms a brown soap; but the hydrous alkalies do not unite with it. It absorbs about 21 times its volume of ammoniacal gas.

When naphtha is passed through a red-hot porcelain tube, it is converted into charcoal, a brown empyreumatic oil, which. when sublimed at the temperature of 95°, yields a portion of colourless crystals in rhomboidal plates, having a lustre similar to that of spermaceti,\* and a quantity of carburetted hydrogen Theodore de Saussure attempted to analyze naphtha by detonating a mixture of the vapour of naphtha and oxygen gas. The result of his experiments was, that 1 volume of vapour of naphtha requires for complete combustion 14 volumes of oxygen gas, and that after the combustion there remain 8.2 volumes of carbonic acid gas. Of consequence 5.8 volumes of the oxygen must have gone to the formation of water, so that the hydrogen in I volume of vapour of naphtha, if in a separate state, would amount to 11.6 volumes. This would make naphtha vapour a compound of

Composition,

8 volumes carbon vapour, condensed into one volume. 12 volumes hydrogen Hence its specific gravity should be 4.1666, and its atomic weight 7.5. It is a compound of 12 atoms hydrogen and 8 So that the atoms are in the proportion of  $1\frac{1}{d}$ atoms carbon. atoms hydrogen to one atom carbon. Thus naphtha differs essentially in its constitution both from alcohol, ethers, and oils.

I subjected naphtha from Persia to analysis by heating it in a copper tube along with peroxide of copper. One grain of naphtha by this treatment yielded 6.5 cubic inches of carbonic acid, and 1.35 grain of water. Now the hydrogen in 1.35 gr. of water is equivalent to 7 cubic inches, and the carbon in 6.5 cubic inches of carbonic acid is equivalent to 6.5 cubic inches.

Hence naphtha is composed of

6.5 volumes of carbon, or 13 volumes,

volumes of hydrogen, 14 volumes.

Substituting atoms for volumes, we have naphtha composed of

<sup>\*</sup> This I consider as the same with the substance first noticed by Mr. · Garden (Annals of Philosophy, xv. 74). I have analyzed it, and found it a compound of 2 atoms carbon + 1 atom hydrogen.

13 atoms carbon	•	•	=	9.75		Sect. VIII.
14 atoms hydrogen	•	•	=	1.75		
·			-	11.50		
	-				Grains.	
61 cubic inches of carbon wei	gh		•	•	0.822	
7 cubic inches of hydrogen	_	i	•	•	0.148	
					~~~~	
					0.970	

So that in this analysis there is a deficiency of three per centwhich I am disposed to ascribe to the presence of azote as a constituent of naphtha in that proportion.\*

2. Sea-wax, or maltha, or mineral tallow, is a solid substance sea-wax. found on the Baikal lake in Siberia. It is white, melts when heated, and on cooling assumes the consistence of white cerate. It dissolves readily in alcohol, and in other respects appears to possess the characters of a solid volatile oil. Its properties, however, have been but imperfectly examined. Klaproth found that a similar substance was obtained by distilling a species of wood coal, called earth coal by the Germans.+

The substance described by Kirwan under the name of mine-low. Mineral tallow, and said to have been found on the coast of Finland, in the Swedish lakes, and in a fountain near Strasburgh, seems to approach very nearly to sea-wax. Its specific gravity is 0.770. It is white, brittle, stains paper like oil, melts when heated, and burns with a blue flame and much smoke; dissolves imperfectly in hot alcohol, but readily in olive oil. Specimens of this substance have been found in different parts of the Highlands of Scotland. There is a specimen in the Hunterian Museum, which was found near Inverary. I have another specimen from a moss in the neighbourhood of Oban. The hatchettine of Conybeare, found in Wales, is merely a variety of mineral tallow.

# 2. Proper Bitumens.

The true bituminous substances may be distinguished by the Characters. following properties:

- 1. They are either solid or of the consistence of tar.
- 2. Their colour is usually brown or black.
- 3. They have a peculiar smell, or at least acquire it when rubbed. This smell is known by the name of the bituminous odour.
  - \* Annals of Philosophy, xv. 307. † Beitrage, iii. 325. ‡ Kirwan's Minefalogy, ii. 47.

. ... . ...

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- 4 They become electric by friction, though not insulated.\*
- 5. They melt when heated, and burn with a strong smell, a bright flame, and much smoke.
- ·6. They are insoluble in water and alcohol, but dissolve most commonly in ether, and in the fixed and volatile oils.
  - 7. They do not dissolve in alkaline leys, nor form soap.
- 8. Acids have little action on them; the sulphuric scarcely any: the nitric, by long and repeated digestion, dissolves them, and converts them into a yellow substance, soluble both in water and alcohol, and similar to the product formed by the action of nitric acid on resins.+

The bitumens at present known may be reduced to three; namely, asphaltum, mineral tar, and mineral caoutchouc. Bitumen has been found also united to a resinous compound, in a curious substance first accurately examined by Mr. Hatchett, to which he has given the name of retinasphaltum. United to charcoal in various proportions, it constitutes the numerous varieties of pit-coal, so much employed in this country as fuel.

Asphaltum,

1. Asphaltum. This substance occurs in great abundance in different countries, especially in the island of Trinidad, on the shores of the Dead Sea, and in Albania, where it is found in vast strata. It is supposed that it was first liquid, and that it acquired solidity by exposure to the air.

Properties.

Its colour is black, with a shade of brown, red, or gray. Its specific gravity varies. That of Albania, as ascertained by Klaproth, was 1.205; that it was somewhat contaminated with earth. Kirwan, in purer specimens, found the specific gravity to vary from 1.07 to 1.165. Klaproth has published an analysis of the asphaltum of Albania.

He found it insoluble both in acids and alkalies, as also in water and alcohol; but soluble in oils, petroleum, and sulphuric ether. Five parts of rectified petroleum dissolved I part of asphaltum, without the assistance of heat, and formed a blackish-brown solution, which by gentle evaporation left the asphaltum in the state of a black-brown shining varnish. The solution in ether was of a pale brown red colour; and when evaporated, the asphaltum remained in the state of a semi-fluid substance of a reddish colour, still insoluble in alcohol.

A hundred grains of this asphaltum being distilled in a retort, by a heat gradually raised to redness, yielded the following products:

<sup>\*</sup> Haüy. † Hatchett. ‡ Beitrage, iii. 315. § Mineralogy, ii. 46.

							Grains.	Sect. VIII.
36 cubic inch	es (Ge	rman	) of he	eavy i	nflam	mable	air 16	
A light brow			•	•	•	•	<b>32</b>	
Water slight			ith am	ımoni	a .	•	6 '	
Charcoal	•	•	•	•	•		30	
Ashes	•	•	•	•	•	•	<b>16</b>	
							<del></del> ·	
		•					100	

These ashes consisted chiefly of silica and alumina, with some iron, lime, and manganese.

The asphaltum found in Albania is supposed to have constituted the chief ingredient of the Greek fire. The Egyptians are said to have employed this bitumen in embalming. It was called mumia mineralis.+ The ancients inform us that it was used instead of mortar in building the walls of Babylon.

2. Asphaltum is seldom absolutely pure; for when alcohol is digested on it, the colour of the liquid becomes yellow, and by gentle evaporation a portion of petroleum is separated. Mineral tar seems to be nothing else than asphaltum contain-Mineral tar. ing a still greater proportion of petroleum. When alcohol is digested on it, a considerable quantity of that oil is taken up; but there remains a black fluid substance like melted pitch, not acted upon by alcohol, and which therefore appears to possess the properties of asphaltum, with the exception of not being solid.§ By exposure to the air, it is said to assume gradually the state of asphaltum.

3. Mineral caoutchouc is a singular substance, hitherto found Mineral caoutchouc. only in Derbyshire. It is soft and very elastic, not unlike common caoutchouc, or Indian rubber, and, like that substance, it may be employed to efface pencil marks from paper; but it soils the paper a little. Its colour is dark brown, sometimes with a shade of green, at other times of red. The first account of it was published by Dr. Lister in the Philosophical Transactions for 1673. It occurred in an old forsaken mine in Derbyshire. He calls it a subterraneous fungus, and is uncertain

- + Watson's Chem. Essays, iii. 4. \* Klaproth's Beitrage, iii. 316.
- ‡ Hatchett's Observations on the Change of some of the Principles of Vegetables into Bitumen. Phil. Trans. 1804.
- § Chemists and mineralogists have united mineral tar to petroleum as a variety. If it be true that pure petroleum is insoluble in alcohol, that arrangement is right; but I suspect a mistake. I had no opportunity of trying naphtha; but the purest petroleum I have been able to procure readily yields to alcohol, unless it has been left exposed to the air.

|| Vol. viii. p. 6179.

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whether it belongs to the vegetable or mineral kingdoms; but rather inclines to the former opinion, and hints that it may have grown out of the old birch props used in the mine. It was first accurately described by Mr. Hatchett. Delametherie first examined its properties; and an analysis of it has been published by Mr. Klaproth.

According to Klaproth, it resists the action of almost all quid menstrua; neither alcohol, alkalies, nor nitric acid, affecting it. Even oils were not found by him to dissolve it, though Delametherie assures us that he obtained a solution of it in olive oil.\* Petroleum succeeded best with Klaproth, assuming a bright yellow colour, while the caoutchouc was rendered transparent.† When heated it melts, takes fire, and burns with a bright flame and a bituminous smell. The melted mass still continues adhesive, and may be drawn out into threads. It is now soluble in oils.‡

One hundred grains of this substance being distilled in a retort gradually raised to a red heat, yielded the following products:

								Grains.
38 cubic in 4 inches	nches ( (Gern	Gern	nan) o of carl	f he <mark>av</mark> oonic	y infla acid s	amma gas	ble air	} 13.75
A brown						•		73.0
Water sli	ghtly a	cidul	ous *	•		•		1.5
Charcoal	•		•		•		•	6.25
Ashes .	•	•		•	•	•	•	5.5
								100:00

The ashes consisted of lime and silica, with some iron, sulphate of lime, and alumina.§

Mr. Hatchett supposes the elasticity of this substance to be owing to a quantity of air confined between its pores.

Retinasphaltum. 4. The retinasphaltum of Mr. Hatchett is a substance hitherto found only accompanying Borey coal, in Devonshire.¶ It was first mentioned by Dr. Milles; but we are indebted to Mr. Hatchett for every thing known respecting its chemical properties.

This substance has a pale brown ochre yellow colour. It is very brittle, and breaks with a vitreous fracture. Its specific

<sup>\*</sup> Jour. de Phys. xxxi. 312. † Beitrage, iii. 109.

<sup>. ‡</sup> Klaproth, ibid. § Ibid. p. 110.

<sup>¶</sup> Unless the substance found near Halle, and analyzed by Bucholz, be similar. See Schweigger's Journal, i. 290.

gravity is 1.135. When held in the hand for some time, it emits a slightly resinous smell. When heated it melts, smokes, burns with a bright flame, and emits a fragrant odour, at last tainted with a bituminous smell. The melted mass, when cold, is black and brittle, and breaks with a glassy fracture.

Water does not act upon it; but it is partially dissolved by alcohol, potash, and nitric acid; the dissolved portion having the properties of a resin; the undissolved of asphaltum. Mr. Hatchett analyzed it, and found it composed of \*

55 resin,41 asphaltum,3 earths.

99

5. Pit-coal, one of the most useful of all the mineral produc- Pit-coal. tions, has been divided by mineralogists into various species, according to its external appearances, and the nature of the strata in which it is found; but in a chemical point of view, its most important varieties may be distinguished into two sets: 1. Those that still contain several vegetable principles, strictly so called, and thus give evident marks of their origin. To this head belong most of the varieties of coal arranged by Werner, under the head of brown coal. Mr. Hatchett has shown, that in some of the substances belonging to this class there is to be found a portion of regetable extract; in others, as in Bovey coal, a portion of resin; besides the charcoal and bitumen, which constitute the greatest part of its constituents. another species of brown coal Klaproth obtained by means of alcohol, a brown red tincture, which left behind it on evaporation, a reddish bitter extract, partially soluble in water.+ Those kinds of coal that contain no traces of unaltered regetable principles, but are composed of various proportions of bitumen and charcoal, contaminated like the former with earthy matter. To this head belong the varieties of coal arranged by Werner under the name of black coal, which abound so much

The different species of black coal which occur in Great species. Britain and Ireland, so far as I have had an opportunity of examining them, are five. They have been distinguished by the following names:

in Britain.

<sup>\*</sup> Hatchett, on the Change of some of the Principles of Vegetables to Bitumen. Phil. Trans. 1804.

<sup>+</sup> Beitrage, iii. 322.

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- 1. Kilkenny coal
- 2. Caking coal,
- 3. Splint coal,
- 4. Cherry coal,
- 5. Cannel coal.

Kilkenny.

1. Kilkenny coal, so called because found at Kilkenny in Ireland, belongs to the Glance coal of Werner. It has a semimetallic lustre; does not soil the fingers. Its specific gravity is 1.4354. It consumes without flame, and, when completely burnt, leaves 4 per cent. of light brown ashes, consisting chiefly of silica and iron.

Caking.

2. Caking coal, is so called because when heated it fuses into a kind of bituminous matter, in consequence of which all the pieces of coal, however small, cohere together into a cake. It occurs abundantly in the neighbourhood of Newcastle and Sunderland, in Fife, at Bannockburn, and in the Glasgow coal formation.

Its colour is velvet black.—Lustre shining, resinous.—Principal fracture straight slaty; cross fracture partly small grained uneven, when the lustre is only glistening; partly small conchoidal when the lustre is shining.—Soft and very easily frangible.—Fragments cubical—brittle—soils the fingers. Specific gravity 1.269. It catches fire very easily, and burns with a lively yellow flame; but in consequence of its caking property, it must be frequently stirred to admit the access of air, otherwise it is extinguished.

Splint,

3. The splint coal occurs abundantly in the neighbourhood of Glasgow, constituting the fifth of the six Glasgow beds. It is a well characterised species, and constitutes the most valuable of the Glasgow coals, selling at a higher price than any of the other species. It is the only coal in the neighbourhood of Glasgow used for the manufacture of coke.

Colour black, with a shade of brown—lustre between glimmering and glistening; resinous—principal fracture imperfect curve slaty. Cross fracture fine grained uneven and splintery—not harder than caking or therry coal, but much more difficultly frangible—fragments wedge shaped—specific gravity 1.290. It requires a much higher temperature to kindle it than either caking or cherry coal. It burns with flame, and is much more durable than cherry coal.

Cherry.

4. Cherry coal abounds in the neighbourhood of Glasgow, and in Staffordshire near Birmingham.

Colour velvet black, with a slight shade of grey; lustre in

some places splendent, in others, shining. Where the lustre Sect. VIII. is shining, the coal has exactly the appearance of caking coal; but it is easily distinguished from that species by not melting or softening when heated-kind of lustre resinous.-Principal fracture straight slaty: the different layers differ in their lustre, some being splendent, others shining. When the lustre is splendent, the surface is specular; but when only shining, it is merely even—cross fracture flat conchoidal, and specular splendent-equally hard with caking coal, and very easily frangible-fragments rectangular-very brittle-specific gravity 1.265. When exposed to heat, it readily catches fire, and burns with a clear vellow flame, and giving out a great deal of heat.

5. Cannel coal is so called, because it burns like a candle cannel. when lighted, and is often employed as a substitute for candles. It abounds at Wigan, is found near Coventry, in Ayrshire, and in Lanarkshire.

Colour dark greyish black; sometimes brownish blacklustre glistening, resinous-admits of a good polish, and is often cut into ornaments like jet. Fracture large and flat conchoidal. In the great it is frequently slaty-fragments sometimes cubic, sometimes wedge shaped, sometimes amorphous.— About as hard as caking coal-brittle-does not soil the fingers—much more difficultly frangible than caking coal or cherry coal; but more easily than splint coal.—Specific gravity 1.272.

The following table exhibits the quantity of earthy matter Ashes. usually found in 100 parts of each of these coals:

ı.	Kilkenny	coal	•	•	4	per cent.
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- 2. Caking coal
- 3. Splint coal 9.5
- 4. Cherry coal 10
- 5. Cannel coal

The following table exhibits the quantity of coke which 1000 coke. parts of each of these species of coal forms.

	Weight of coal em- ployed	Weight of coke formed,	• Volatile matter dis- sipated,	Weight of coal, ex- cluding ashes.	Weight of coke, excluding ashes.	Volatile matter.
Kilkenny coal	1000	867·0	133·0	1000	861·4	138·6
Caking coal	1000	774·0	226·0	1000	770·6	229·4
Splint coal	1000	647·3	352·7	1000	610·3	389·7
Cherry coal	1000	522·5	477·5	1000	469·4	530·6
Cannel coal	1000	400·0	600·0	1000	325·8	674·2

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I determined the constituents of these different species by heating them in contact with peroxide of copper. The following tables exhibit the result of these experiments.\*

## 1. Constituents by weight.

Composition.

4	Carbon.	Hydrogen.	Azote,	Oxygen,	Total.
Kilkenny coal	92·92	0·00	0.00	7·08	100
Caking coal	75·28	4·18	15.96	4·58	100
Splint coal	75·00	6·25	6.25	12·50	100
Cherry coal	74·45	12·40	10.22	2·93	100
Cannel coal	64·72	21·56	13.72	0·00	100

## 2. Constituents in atoms.

	Carbon.	Hydrogen,	Azote.	Oxygen.	Total number of atoms.
Kilkenny coal	35	0	0	2	37
Caking coal	33	11	3	1.5	48.5
Splint coal	28	14	1	31	46.5
Cherry coal	34	34	2	1	71
Cannel coal	11	22	1	0	34

<sup>\*</sup> Annals of Philosophy, xiv. 81.

# PART III.

## OF SECONDARY COMPOUNDS.

By secondary compounds, is meant the compounds formed by the union of the primary compounds with each other. Now—as the neutral primary compounds enter into but few combinations, it is obvious that the secondary compounds must consist chiefly of combinations of the acids with the bases. Such compounds are called salts. They constitute a very numerous and important set of bodies, which it is of great consequence to understand well.

The word salt was originally confined to common salt; a Salt, what substance which has been known and in common use from the remotest ages. It was afterwards generalized by chemists, and employed by them in a very extensive and not very definite sense. Every body which is sapid, easily melted, soluble in water, and not combustible, has been called a salt.

Salts were considered by the older chemists as a class of bodies intermediate between earths and water. Many disputes arose about what bodies ought to be comprehended under this class, and what ought to be excluded from it. Acids and alkalies were allowed by all to be salts; but the difficulty was to determine concerning earths and metals; for several of the earths possess all the properties which have been ascribed to salts, and the metals are capable of entering into combinations which possess saline properties.

In process of time, however, the term salt was restricted to three classes of bodies; namely, acids, alkalies, and the compounds which acids form with alkalies, earths, and metallic oxides. The first two of these classes were called simple salts; the salts belonging to the third class were called compound or neutral. This last appellation originated from an opinion long entertained by chemists, that acids and alkalies, of which they are composed, were of a contrary nature, and that they counteracted one another; so that the resulting compounds possessed neither the properties of acids nor of alkalies, but properties intermediate between the two.

Chemists have lately restricted the term salt still more, by tacitly excluding acids and alkalies from the class of salts alto-

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gether. At present, then, it denotes only the compounds formed by the combination of acids with alkalies, earths, and metallic oxides.\*

As there are nine classes of acids, it is obvious that there must be as many classes of salts. I shall give an account of these different classes in succession.

#### CLASS I.

### OXYGEN ACID SALTS.

Nomenclature.

This class of salts has been longest known and most completely investigated. Of course the salts belonging to it are by far the most numerous. According to the nomenclature introduced by Morveau, which is still followed in chemistry, the genera of these salts are named from their acid. Thus if the acid be sulphuric the salt is called a sulphate, if the acid be the nitric the salt is called a nitrate, and so on. The species are distinguished from each other by adding the name of the base. Thus sulphate of soda is a salt composed of sulphuric acid and soda; oxalate of lime is a salt composed of oxalic acid and lime. When the salt is a compound of one atom of acid with one atom of base, it is distinguished simply by the name. If the salt contains two atoms of acid united to one atom of base, the Latin numeral adverb bis or bi is prefixed. Thus bisulphate of potash is a salt composed of two atoms sulphuric acid and one atom potash. Were there 3, 4, &c. atoms acid, the numeral adverbs ter, quater, &c. would be prefixed. Thus quateroxalate of potash means a compound of 4 atoms oxalic acid and 1 atom potash. When there exists an atom and a half of acid united to one atom of base, the Latin term sesqui (one and a half) is prefixed. Thus sesquicarbonate of soda is a compound of 11 atom carbonic acid with 1 atom soda.

When two atoms of base are combined with one atom of acid this is denoted by prefixing the Greek numeral adverb dis. Thus diphosphate of potash means a compound of two atoms potash with one atom phosphoric acid. The prefixes tris, tetrakis, &c. indicate three, four, &c. atoms of base with one atom of acid.

After considering the subject with considerable attention, I

<sup>\*</sup> The terms salt and neutral salt are often confounded. In this work the epithet neutral is confined to salts having no excess of acid or base.

think the mode of arranging the salts according to the bases is attended with such advantages as to induce me to adopt it in this work. We should therefore divide this class into 42 sections. allowing a section for the salts formed by the combination of each salifiable base with the different acids. But there are several of the acid bases which combine with acids and form salts. This, together with the double salts, will oblige us to divide the class into no fewer than 52 sections.

Class 1.

### SECTION I. -SALTS OF AMMONIA.

- 1. The salts of ammonia, with a very few exceptions, are all soluble in water.
- 2. When potash or quicklime is mixed with an ammoniacal Characters. salt, a smell of ammonia is emitted.
- 3. If to an ammoniacal salt dissolved in water a little salt containing magnesia be added, and afterwards some phosphate of soda dropped in, a copious white precipitate falls.
- 4. When an ammoniacal salt is exposed to heat it is completely dissipated in vapours; except when the acid has a fixed metal, or phosphorus, or boron for its base, in which last case the acid alone remains behind.
- 5. The ammoniacal salts are not precipitated by infusion of nut-galls or prussiate of potash.
- 6. When a solution of platinum is dropped into a salt of ammonia, a yellow coloured precipitate falls in very small crystals.

This genus of salts has been very fully investigated. following are the different species:

Sp. 1. Sulphate of ammonia. This salt was discovered by Sulphate of ammonia. Glauber, and called by him secret sal ammoniac. It was also called vitriolated ammoniac. It may be prepared by saturating ammonia with sulphuric acid, or by decomposing sal ammoniac by means of sulphuric acid. It exists native, and is then distinguished by the name of muscugnin. There are two subspecies of this salt, differing from each other in the water of crystallization.

(1.) Proto-hydrated sulphate. I obtained it crystallized in regular rectangular plates, and consider the form of the crystal to be a four-sided prism with square bases. It is transparent and colourless. Its specific gravity is 2. It has a sharp bitter taste. It is soluble in twice its own weight of water at the temperature of 60°, and in its own weight of boiling water. Water of the temperature of 144° dissolves 0.78 of its weight

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of this salt.\* When exposed to the air, it slowly attracts moisture. Indeed from the experiments of Hatchett it is obvious that at a red heat the salt is completely decomposed. I found this variety composed of

1 atom sulphuric a	acid	•	•	5
1 atom ammonia		•	•	$2 \cdot 125$
1 atom water	•	**	•	1.125
				8.25

(2.) Deuto-hydrated sulphate. From the analyses of Kirwan and Berzelius it appears that this variety is the most common state of the salt, in which it is obtained when dilute sulphuric acid is saturated with carbonate of ammonia, and the liquid after being sufficiently concentrated is set aside to crystallize. The crystals seem to have exactly the same shape as those of sulphate of potash. In other respects, its properties agree with those of the preceding variety. I have never, however determined its specific gravity. From the analysis of Berzelius, its constituents are

1 atom sulp	huric acid	•	•	5
1 atom amm	onia .	•	•	$2 \cdot 125$
2 atoms wat	er .	•	•	2.25
			•	9:375

By drying it on the sand bath it loses one atom of water, and is converted into the first variety.

Bisulphate.

2. Bisulphate of ammonia. This salt is easily formed by dissolving the preceding in water acidulated with a quantity of sulphuric acid equal to that which the salt contains, and then evaporating the solution to the proper consistency. The bisulphate crystallizes in thin rhomboidal plates. It has an acid and bitter taste. When exposed to the air it speedily attracts moisture and deliquesces. It is soluble in its own weight of cold water. It is a compound of two atoms sulphuric acid and one atom ammonia, but I have not determined the water of crystallization which it contains.

Sulphite.

3. Sulphite of ammonia. This salt is easily obtained by passing a current of sulphurous acid through a solution of ammonia in a Woolfe's bottle. The salt may be obtained crys-

tallized in six-sided prisms. Its taste is cooling, sharp, and sulphureous. When heated it decrepitates, and becomes white without melting, giving out a little ammonia and being converted into a bisulphite. It dissolves in its own weight of water. It has not been analyzed, but is probably a compound of

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1 atom sulphurous acid. 1 atom ammonia 2.125  $\frac{1}{2}$  atom water • 0.5625

6.6875

4. Hyposulphite of ammonia. According to Mr. Herschell, blite. the only person who has hitherto examined this salt, it is always a compound of 2 atoms acid with 1 atom base; so that it is a bihyposulphite. It does not readily crystallize; but when much concentrated, cools into a confused pappy mass of very minute spiculæ. Its taste is bitingly pungent, succeeded by a disgusting bitterness. When heated, it burns with a weak flame, and evaporates entirely.\*

5. Hyposulphate of ammonia. This salt was formed by M. Hyposulphate Heeren of Hamburgh, by decomposing hyposulphate of barytes by means of sulphate of ammonia. It is so soluble in water that he was unable to obtain it in regular crystals. By spontaneous evaporation some needle-shaped crystals appeared. At the temperature of 60° it dissolves in 0.79 of its weight of water. During the solution the temperature sinks considerably. It is insoluble in absolute alcohol: The taste is cooling, and similar to that of Glauber salt. When heated, it gives off water without melting, then sulphurous acid is expelled, and the residue (which now melts) is sulphate of ammonia. Its constituents, as determined by the analysis of M. Heeren, are

1 atom acid 1 atom ammonia 2.125 2 atoms water

6. Nitrate of ammonia. This salt has been long known: it Nitrate. was formerly distinguished by the names of nitrum semivolatile and nitrum flammans. Berthollet examined it in the course of his experiments on the component parts of nitric acid; and Sir H. Davy has added considerably to our knowledge of its composition and decomposition.† It may be prepared by dis-

13.375

<sup>\*</sup> Edinburgh Phil, Jour. i. 19.

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solving carbonate of ammonia in diluted nitric acid, and evaporating the solution till the salt crystallizes.

The appearance of this salt varies very much, according to the temperature at which its solution is evaporated. In a moderate heat, 70° or 100° for instance, and by slow cooling, it is obtained in six-sided prisms, terminated by long six-sided pyramids. When the solution is evaporated at the temperature of 212°, the crystals are channelled and have a fibrous texture, or they are formed of long soft elastic threads. When dried in a heat of about 300°, it assumes the form of a white compact mass. These differences are owing to different proportions of water of crystallization which the salt contains.

Nitrate of ammonia has a very acrid, bitter, disagreeable taste. Its specific gravity is 1.5785.\* At the temperature of 60° this salt is soluble in two parts of water: it dissolves in half its weight of boiling water.† It must be observed, however, that its solubility varies with the proportion of water of crystallization which it contains. When exposed to the air, nitrate of ammonia soon attracts moisture and deliquesces.

When this salt, in the state of fibrous or prismatic crystals, is heated, it becomes fluid at a temperature below 300°; between 360° and 400° it boils without decomposition; but when heated to 450°, or somewhat higher, it is gradually decomposed without losing its water of crystallization. Compact nitrate, on the other hand, undergoes little or no change till it is exposed to a temperature higher than 260°. Between 275° and 300° it sublimes slowly without decomposition, and without becoming fluid. At 320° it melts, and at the same time is partly decomposed, partly sublimed.‡

When this salt is decomposed in a temperature not exceeding 500°, it is wholly converted into protoxide of azote and water. From the experiments of Davy, it appears that these products are nearly in the proportion of four parts of gas to three parts of water.§ It is easy to see that (abstracting the water of crystallization) it must be decomposed into

Water . . . 3.375 or 30 Protoxide of azote . . 5.5 44

Now this is nearly in the proportion of 3 parts of water to  $4\frac{1}{2}$  parts of protoxide of azote. When it is exposed to a heat above 600°, this salt explodes, and is totally decomposed, being

<sup>\*</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

<sup>†</sup> Fourcroy, iii. 195, Eng. Trans.

<sup>‡</sup> Davy, p. 85. § Ibid. p. 105.

converted into nitrous acid, nitrous gas, water, and azotic gas. This phenomenon, observed long ago, induced the older chemists to give the salt the name of nitrum flammans. The nature of the decomposition was first ascertained by Berthollet, and more lately it has been examined by Davy. Its constituents, as determined by Berzelius,\* afterwards confirmed by an analysis of my own,† are as follows:

Sir H. Davy analyzed the salt in crystals, in a fibrous, and in a prismatic state; the results were as follows:

The proportion of ammonia is too small in all of these analyses. But if we make allowance for this defect, the composition in atoms will be nearly as follows:

- 7. Hyponitrite of ammonia. This salt is obtained when Hyponitrite. hyponitrite of lead and sulphate of ammonia are dissolved in water and mixed in the atomic proportions. The solution when evaporated gives an irregularly crystallized mass, containing one atom of water. When heated to 122° it gives out azotic gas (according to Berzelius),‡ and is converted into nitrate of ammonia.
- 8. Carbonate of ammonia. This salt has been long known. Carbonate. It is often obtained by distilling animal substances: but for chemical purposes it is best to extract it from sal ammoniac by means of chalk. Two parts of chalk and 1 part of sal ammoniac, both as dry as possible, are mixed together and put into an earthen retort. On the application of a sufficient heat, carbonate of ammonia sublimes, and is obtained in the state of a white crystallized mass. The crystals are so small and so irre-

<sup>\*</sup> Ann. de Chim. lxxx. 182. † First Principles, ii. 240. † Gilbert's Annalen, xl. 206.

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1 atom carbonic	acid	•	۰.	2.75
1 atom ammonia	a .	•	•	$2 \cdot 125$
1 atom water	•	•	•	1.125
				6.

Sesquicarbonate.

9. Sesquicarbonate of ammonia. This is the name which ought to be applied to the carbonate of ammonia of the shops. It is in hard white cakes, about two inches thick, and is evidently obtained by sublimation. At least I have never met with any of these cakes that did not contain an excess of carbonic acid. Its constituents, from a careful analysis made in my laboratory, were found to be

$1\frac{1}{2}$	atom	acid	•	•	•	4.125
1	atom	ammon	ia	•	•	2.125
1	atom	water	•	•	•	1.125
						<del></del>
						7.375

The carbonate may be formed by mixing

1 volume carbonic acid gas,

2 volumes ammoniacal gas,

1 volume vapour of water.

The sesquicarbonate by mixing

11 volume carbonic acid gas,

2 volumes ammoniacal gas,

volume vapour of water.

Bicarbonate.

10. Bicarbonate of ammonia. This salt may be obtained by exposing the common carbonate of ammonia in powder to the air, or by causing a current of carbonic acid gas to pass through a solution of it in water. It crystallizes in six-sided prisms,

<sup>\*</sup> Bergman, i. 21. + Hassenfratz, Ann. de Chim. xxviii. 12.

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usually small, has no smell, and less taste than the carbonate. It dissolves in 8 times its weight of cold water. Berthollet has shown that when the solution is slightly heated the salt loses a portion of its acid. It was analyzed by Schrader, \* Berthollet,† and Phillips,‡ from the result of whose analyses it is obvious that its constituents are

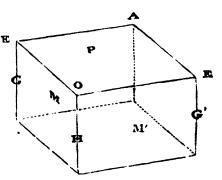
2 atoms carbonic	acid	•	•	<b>5·5</b>
1 atom ammonia	• .	•	•	2.125
2 atoms water	•	•	•	2.25
				9.875

11. Phosphate of ammonia. This salt exists in urine, and seems to have been first accurately distinguished by Rouelle. It was afterwards examined by Lavoisier in 1774, and still more lately by Vauquelin.§ It is usually prepared by saturating with ammonia the superphosphate of lime obtained from bones, and evaporating the solution to such a consistency, that when allowed to cool the phosphate of ammonia is obtained in crystals. For the most complete examination of phosphate of ammonia, we are indebted to Mitcherlich.

The crystals which form (if we leave the saturated solution to spontaneous evaporation) are large and transparent. After the crystals have been deposited the solution is usually acid.

The shape of the crystals is an oblique rhombic prism, in which M on M' is an angle of 84° 30', and P on M 105° 23'. In the crystals the angle  $\Lambda$ , is often replaced by a face, making

the summit of the prism consist of two faces like the roof of a house. This new face makes with P an angle of 109° 44′. Sometimes the angles E, E', and O, are also replaced by small triangular faces. When these crystals are exposed to the air, they effloresce, and at the same time lose a portion of their ammonia,



so that they are at last converted into biphosphate of ammonia. Its taste is saline and cooling, with an impression of bitterness. It dissolves in four times its weight of cold water, but is doubt-

11. 2 c

<sup>\*</sup> Gehlen's Jour. ii. 582. † Gehlen's New Algem. Jour. iii. 255.

<sup>‡</sup> Annals of Philosophy (2d series), i. 110.

<sup>§</sup> Jour. de l'Ecole Polytechnique.

<sup>||</sup> Ann. de Chim. et de Phys. xix. 382.

less more soluble in hot water. When heated it melts, and gradually loses its ammonia and part of its water, and is converted into hydrated phosphoric acid. Its constituents, as determined by Mitcherlich, are

1 atom phosphoric acid..4.51 atom ammonia..2.125 $1\frac{1}{2}$  atom water..1.6875

8.3125

I obtained 2 atoms of water; but as the analysis was made simply by precipitating the acid by means of nitrate of lead, the result is somewhat uncertain.\* On that account I rather prefer the experiment of Mitcherlich.

12. Biphosphate of ammonia. This salt is easily obtained by adding phosphoric acid to a solution of phosphate of ammonia, till it strongly reddens litmus paper, and ceases to precipitate muriate of barytes. When the solution is concentrated it crystallizes readily in octahedrons with square bases, having most commonly a four-sided right prism interposed between the two pyramids. This is the salt that has been longest known, and which is described in older chemical books under the name of phosphate of ammonia.

Its crystals are transparent, and undergo no alteration by exposure to the air. The taste is acid, and cooling, and saline. When heated it melts and swells up greatly from the conversion of the water into vapour, and the extrication of the ammonia. By continuing the heat nothing remains at last but hydrated phosphoric acid.

I found that 9.125 grains of this salt were decomposed by 41.5 grains of nitrate of lead. From this I concluded that the salt is anhydrous.† But this mode of analysis cannot be depended on. There is no doubt that it contains water; because that liquid is disengaged when the salt is heated. Mitcherlich's analysis, assisted by a little calculation, gives its constitution as follows:

2 atoms phosphoric a	ıçid	•	•	9
l atom ammonia	•	•	•	2.125
3 atoms water	•	•	•	3.375

14.5

13. Phosphite of ammonia may be obtained by saturating

<sup>\*</sup> First Principles, ii. 245. † Ibid. p. 246.

phosphorous acid with carbonate of ammonia. When concentrated to the consistence of a syrup, it yields large crystals, which are very deliquescent. When heated it gives out ammonia, and the phosphorous acid and water remain as if they had not been combined with ammonia. When the heat is increased, this acid is decomposed in the usual way, and at last a hydrated phosphoric acid remains.\* It has not been analyzed, but from the phenomena of its decomposition there can be little doubt that its constituents are

1 atom phosphorous	acid		•	3.5
1 atom ammonia	•	•	•	$2 \cdot 125$
2 atoms water	_	_		2.25

7.875

There is also a biphosphite of ammonia, but it has not been particularly examined.

- 14. Hypophosphite of ammonia. This salt has been examined only by Dulong. It is very deliquescent, and dissolves very readily in water and absolute alcohol.
- 15. Arseniate of ammonia. This salt may be prepared by adding ammonia to a concentrated solution of arsenic acid till a precipitate appear. This precipitate is dissolved by heat, and the liquid being set aside, deposites large crystals of arseniate of ammonia.

Mitcherlich has shown that the salt resembles phosphate of ammonia so closely, that we cannot distinguish them from each other by their external characters. They have the same taste, and the crystalline shape is the same, an oblique rhomboidal prism. The angles differ a very little from those of phosphate of ammonia, but not so much that the difference can be detected by the eye. The measurements of arseniate of ammonia are as follows:

M on M' 85° 54', or 1° 24' greater than in phosphate of ammonia.

P on M 105° 46', or 23' greater than phosphate of ammonia. f (the face on A) on P 109° 6', or 38' less than in phosphate of ammonia.

When heated, ammonia is given out, then water, while at last arsenic sublimes, and azotic gas is extricated. When this salt is exposed to the air it loses half its ammonia, and is converted into binarseniate of ammonia.

According to the analysis of Mitcherlich its constituents are

<sup>\*</sup> H. Rose, Poggendorf's Annalen, ix. 28.

Class	T.
✓ 1000	20

1 atom arsenic acid	•	•	7.25
1 atom ammonia	•	•	$2 \cdot 125$
$l_{2}^{1}$ atom water	•	•	1.6875
			11.0625*

My analysis was not sufficient to determine the true constitution of this salt, as it was made simply by precipitation.

16. Binarseniate of ammonia. This salt is easily formed by adding to a solution of the preceding salt an additional dose of acid, and then crystallizing, or simply by exposing the preceding salt for some time to the open air, and then dissolving it in water and crystallizing.

Mitcherlich has shown that it resembles the biphosphate of ammonia perfectly in its properties. The description of the one, therefore, applies to the other. The shape of the crystals is the same. Its constituents, according to the analysis of the same chemist, are

2 atoms arsenic acid	•	•	14.5
1 atom ammonia	•	•	2.125
3 atoms water	•	•	3.375
			20·000t

17. Borate of ammonia. It appears from an analysis by Berzelius, § that this salt may be formed and obtained in crystals; but no description of it has been made. He found the constituents as follows:

Boracic acid	•	•	<b>37</b> ·9 <b>5</b>
Ammonia	•	•	30.32
$\mathbf{W}$ ater	•	•	31.73

100.00

He has since stated that this analysis is not quite accurate. || It comes nearest to

1 atom boracic acid			3
l atom ammonia	•	•	2.125
2 atoms water	•	•	2.25

7.375

## 18. Sesquiborate of ammonia. Arfvedson formed this salt and

<sup>\*</sup> Ann. de Chim. et de Phys. xix. 384.

<sup>†</sup> First Principles, ii. 246. † Ann. de Chim. et de Phys. xix. 373.

<sup>§</sup> Annals of Philosophy, iii. 57. | Poggendorf's Annalen, ii. 126.

subjected it to analysis; but he has not given any description

sect. 1.

of it. He found the constituents as follows:

Boracic acid	•	•	55.95
Ammonia	•	•	21.55
Water .		•	22.50
			100.00*

This is obviously the same as

 1½ atom boracic acid
 .
 4.5

 1 atom ammonia •
 .
 2.125

 2 atoms water
 .
 .

8.875

19. Terborate of ammonia. This salt may be formed by adding boracic acid to a warm aqueous solution of ammonia in the atomic proportion, and then allowing the solution to cool. It crystallizes in octahedrons with rhombic bases, like sulphur, but shorter, and the apices are usually truncated. In the air it effloresces, and gradually becomes sexborate by losing ammonia. It dissolves in about 12 times its weight of cold water. When the solution is heated, ammonia is disengaged. We have the three following analyses of this salt:

			100.0+		100.001		99.996
Water	•	•	<b>36·5</b>	•	23.78	٠	36.452
Boracic acid	•	•	51.0	•	63.34	•	50.000
Ammonia	•	•	12.5	•	12.88	•	13.544

These agree best with

 3 atoms boracic acid
 .
 9

 1 atom ammonia
 .
 2·125

 5 atoms water
 .
 5·625

16.75

20. Sexborate of ammonia. This salt may be formed by saturating warm liquid ammonia with boracic acid, and allowing the solution to cool slowly. The crystals are transparent and irregular; but seem to be four and six-sided prisms, usually terminated by pyramids. The taste is at first very slight, but

<sup>\*</sup> Poggendorf's Annalen, ii. 130.

<sup>+</sup> L. Gmelin, Handbuch, i. 472.

<sup>‡</sup> Arfvedson, Poggendorf's Ann. ii. 130.

<sup>§</sup> Soubeiran, Jour. de Pharm. xi. 34.

Close	T
Class	ı.

a bitter impression is left in the mouth. Like all the salts of boracic acid it acts as an alkali. We have three analyses of this salt, the results of which are as follows:

Ammonia	•	•	5.9	•	7.9	•	7.24
Boracic acid	•	•	$63 \cdot 4$	•	64.0	•	<b>55</b> ·80
Water	•	•	30.7	•	28.1	•	36.96
			100.0*	ŧ	100.0	<b>}</b>	100.00‡
These agree bes	t with						
6 atom	s bora	cic acid		•	18		

T

2.125 1 atom ammonia 7 atoms water 7.875

28

It is therefore a sexborate of ammonia.

- 21. Silicate of ammonia. When newly precipitated silica is digested in an aqueous solution of caustic ammonia, a considerable portion of it is dissolved. But carbonate of ammonia dissolves very little of it.§
  - 22. Seleniate of ammonia. Not yet described.
- 23. Selenite of ammonia. This salt is obtained by adding selenious acid to concentrated caustic ammonia till there be a small excess of acid. When the solution is left in a cool place, the salt precipitates partly in four-sided prisms, and partly in feather shaped crystals. They deliquesce when exposed to the air.
- 24. Biselenite of ammonia is formed when the neutral selenite is dissolved in water, and the liquid is left to spontaneous evaporation. A portion of the ammonia flies off, and the biselenite is deposited in acicular crystals, which undergo no change, though exposed to the air.
- 25. Quaterselenite of ammonia is obtained either by heating a solution of biselenite, or by adding selenic acid to the bise-It does not crystallize, and when evaporated to dryness, speedily absorbs moisture from the atmosphere.
- 26. Antimoniate of ammonia. This combination has hitherto been examined by Berzelius only. It may be formed by digesting the hydrate of antimonic acid in caustic ammonia.

<sup>\*</sup> L. Gmelin, Schweigger's Jour. xv. 258.

<sup>+</sup> Arfvedson, Poggendorf's Ann. ii. 130.

<sup>‡</sup> Soubeiran, Jour. de Pharm. xi. 34.

<sup>§</sup> Karsten, Poggendorf's Annalen, vi. 357.

Berzelius, Ann. de Chim. et de Phys. ix. 260.

A neutral solution is gradually formed. If we attempt to evaporate it a portion of the ammonia is disengaged and a white powder falls, which is a superantimoniate of ammonia. It reddens vegetable blues, and when heated in a retort ammonia and water are driven off, and antimonic acid remains behind. This supersalt is not decomposed by exposure to the air for months, even at the temperature of 122°.\*

- 27. Antimonite of ammonia. If the antimonious acid be digested in caustic ammonia a solution is obtained. When this solution is exposed to the air a white precipitate falls, which is a binantimonite of ammonia.
- 28. Tellurate of ammonia. When oxide of tellurium is digested in caustic ammonia a solution is obtained. An acid dropped into this solution precipitates a white powder, which is a bitellurate of ammonia.†
- 29. Chromate of ammonia. This salt may be formed by saturating chromic acid with ammonia, and concentrating the solution under the exhausted receiver of an air-pump over sulphuric acid. The salt is gradually deposited in crystalline scales. It has a fine yellow colour, a hot and saline taste. It reacts upon vegetable blues like an alkali.‡ It is exceedingly soluble in water, and the solution cannot be concentrated by heat without depriving the salt of half of its ammonia. I found it anhydrous, and composed of

30. Bichromate of ammonia is always obtained when we concentrate the solution of the preceding salt on the sand bath. The bichromate is deposited in beautiful crystalline plates, which are not altered by exposure to the air. It has a fine red colour. The taste is hot, bitter, and very disagreeable. It reddens vegetable blues, and is very soluble in water. The primary figure of its crystals,

according to Mr. Brooke, § is an oblique rhombic prism, having its edges replaced with faces as represented in the margin. The following are the measurements of the principal angles.



<sup>‡</sup> I have however obtained it in a state incapable of giving a blue colour to reddened litmus paper.

<sup>§</sup> Annals of Philosophy (2d series), vi. 287.

P on M or M'	•	•	114°
M on M'.	•	•	98° 8′
P on h .		•	122° 31′
M on h .	•	•	139° 4′
Mong.		•	135° 47′

When heated, it melts, and loses its water and ammonia; a dark green matter remains, which speedily becomes solid, exhibiting the rudiments of crystallization on the surface. This matter is brittle, has a cooling and sharp taste, and partly dissolves in water, forming a deep yellow solution, and partly remains in the state of a deep green insoluble matter. This matter seems to be a chromate of chromium. This salt, by my analysis, is a compound of

2	atoms chromic	acid	•	•	13
1	atom ammonia	•	•	•	2.125
2	atoms water	•	•	•	2.25
					<del></del>
					17:375

31. Molybdate of ammonia. This salt is formed when molybdic acid is digested in caustic ammonia to saturation. When the filtered solution is set aside, crystals of molybdate of ammonia are gradually deposited. These crystals are irregular four-sided rectangular prisms. The taste of the salt is bitterish, saline, and metallic. When heated, it gives out water, ammonia, and azote, and leaves a brown oxide or molybdic acid, according to the degree of heat. It dissolves in about twice its weight of water, and when the aqueous solution is concentrated it gives out ammonia. It has not been rigidly analyzed, but from the experiments of Brandes, there is reason to consider it as a compound of

1	atom	molybdic	acid	•	•	9
1 :	atom	ammonia		•	•	$2 \cdot 125$
1 0	atom	water		•	•	0.5625

## 11.6875

32. Bimolybdate of ammonia. When the solution of the preceding salt is concentrated by heat, half the ammonia is driven off, and when the concentrated solution is set aside, large crystals of bimolybdate of ammonia make their appearance, the shape of which has been described by Haidinger.\* When heated, they give out ammonia, water, and azote, and

leave an ash grey substance, the nature of which has not been investigated.

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33. Bitungstate of ammonia. This salt may be formed by dissolving tungstic acid in caustic ammonia. When the concentrated solution is set aside, small white crystals are deposited, composed of four-sided prisms, and very little soluble in water. It has a sharp, bitter, metallic taste. Its constituents are

2 atoms tungstic acid	•	•	31
1 atom ammonia .	•	•	2.125
2 atoms water • .	•	•	$2 \cdot 25$
_			•
-			35.375

There is another tungstate of ammonia, much more soluble in water, which is probably a neutral tungstate, but it has not yet been analyzed.

- 34. Titaniate of ammonia. When ammonia is poured into the milk consisting of hydrated titanic acid and water, flocks immediately separate, which are easily collected on the filter.\* These flocks probably constitute a titaniate of ammonia.
- 35. Columbate of ammonia. When the hydrate of columbic acid is digested in caustic ammonia, a combination is formed, which remains solid and does not redden litmus paper. From this compound the ammonia is easily expelled by heat, or even by simple exposure to the air. By means of this salt other columbates may be formed by double decomposition.† Columbic acid is very little soluble in carbonate of ammonia.
- 36. Uraniate of ammonia. When nitrated peroxide of uranium in solution is decomposed by ammonia a yellow powder falls, which is a uraniate of ammonia. This salt may be exposed to a heat of 212° without alteration. When the heat approaches to redness it is decomposed, ammonia and azotic gas being driven off and protoxide of uranium remaining. It is slightly soluble in water, but not in liquid ammonia. From my trials on it I consider it as a compound of

1	atom	peroxide	of	ura	mium		28
1	atom	ammonia	•	•	•	•	$2 \cdot 125$
$1_{2}^{1}$	atom	water	•		•	•	1.6875

31.8125

37. Oxalate of ammonia. This well-known and very useful salt is obtained by saturating a solution of oxalic acid with

<sup>\*</sup> II. Rose. + Gahn, Berzelius, and Eggertz.

carbonate of ammonia, and after concentrating the liquid setting it aside for crystallization. The crystals are usually needle form. But they may be obtained in right rhombic prisms, the faces of which are inclined at angles of 104° 7′. The longitudinal edges of the prism are often replaced by tangent planes, while the angles at the base are also often replaced by one or two small faces.\*

The taste of this salt is bitter and unpleasant, somewhat like that of sal ammoniac. The specific gravity of the crystals is 1.582. At the temperature of 60? 100 parts of water dissolve only 4.5 parts of this salt. The specific gravity of the solution is 1.0186. This salt is insoluble in alcohol. When distilled, carbonate of ammonia is disengaged, a little of the acid is sublimed, and a residuum of charcoal remains behind. This salt is much used as a reactive to detect the presence of lime.†

When heated it gives off one atom water, and is converted into a white opaque mass. By a higher temperature it is completely decomposed. Its constituents are

1 atom oxalic acid		•	4.5
l atom ammonia	•	•	$2 \cdot 125$
2 atoms water	•	•	2.25

8.875

38. Binoxalate of ammonia. This salt may be formed by adding oxalic, sulphuric, nitric, or muriatic acid to a solution of oxalate of ammonia and setting the solution aside (sufficiently concentrated) for crystallization.

The crystals of this salt are sometimes octahedrons, but most commonly rectangular flat four-sided prisms, having two opposite lateral edges replaced by tangent planes. The taste of the salt is acid. It reddens vegetable blues, and is not altered by exposure to the air. I found the constituents of this salt

2 atoms oxalic acid	•	•	9
1 atom ammonia.	•	•	2.125
8 atoms water			9

20.125

## 39. Acetate of ammonia. This salt has been long employed

<sup>\*</sup> Mr. Brooke has given a description of the crystals in the Annals of Philosophy (second series), vi. 374.

<sup>+</sup> Bergman, i. 261.

in medicine under the name of spiritus mindereri. It is easily prepared by saturating acetic acid with carbonate of ammonia. If we put the saturated solution under the exhausted receiver of an air-pump over sulphuric acid, the acetate crystallizes in transparent oblique rhomboidal prisms. The faces are striated, and the salt so deliquescent, that they cannot be measured. impresses the tongue at first with a sense of coldness, and then of sweetness, which is followed by a taste resembling that of a mixture of sugar and nitre, in which the sweet does not predominate over the mawkish taste of the nitre.\* It melts at 170°, and sublimes at about 250°.† When a watery solution of this salt is distilled, there comes over first a quantity of ammonia, next a quantity of acetic acid, and at last of the salt itself containing an excess of acid. No such decomposition takes place when the crystals are distilled by a moderate heat. ‡ According to my trials, 40 grains of the crystals dissolved in water and digested over calcareous spar in powder, dissolve 15.5 grains of carbonate of lime. From this it follows that the salt is composed of

1	atom acetic acid	•	•	6.25
1	atom ammonia	•	•	2.125
7	atoms water	•	•	7.875

16.25

- 40. Binacetate of ammonia. When the aqueous solution of the preceding salt is heated it gives out half of its ammonia. If the heat be continued the binacetate sublimes in needleform crystals. The same salt may be obtained by heating a mixture of acetate of potash or lime and sal ammoniac. This salt deliquesces when exposed to the air. Its taste is sour, and it reddens vegetable blues.
- 41. Formate of ammonia. This salt has been but imperfectly examined. It crystallizes in right rectangular prisms, usually terminated by four-sided pyramids. It is readily soluble in water, and may be sublimed without decomposition. According to Dobereiner, when strongly heated it is decomposed into water and hydrocyanic acid.
- 42. Mellate of ammonia. This salt is formed when mellite is boiled in a solution of carbonate of ammonia. The concentrated solution readily yields crystals of mellate of ammonia. They are transparent and colourless, and the salt crystallizes in two different forms, which have been described and figured by

<sup>\*</sup> Higgins on Acetous Acid, p. 192. † Ibid. † Ibid.

- G. Rose.\* The first is a rhomboidal prism, whose faces are inclined to each other at angles of 119° 41′, while in the other the inclination is 114° 16′. The first terminates by a four-sided pyramid, whose faces are set on the lateral faces of the prism, and whose apices are truncated; while the other terminates in two faces rising from the angle of the prism terminating the obtuse inclination. The first kind of crystal remains sometime unaltered in the air, and then becomes milk white and opaque without losing its shape. The second form becomes opaque instantly when taken out of the solution, and even while still moist. Wöhler, who observed these alterations, does not consider them as owing to the escape of water, but to a new arrangement of the particles of the crystal.† Indeed this change in the appearance of the salt by exposure had been noticed by Klaproth.‡
- 43. Tartrate of ammonia. The crystals of this salt are polygonous prisms, not unlike those of tartrate of soda. It has a bitter taste like that of nitre. It is very soluble in water. Heat decomposes it. Its constituents are

- 44. Bitartrate of ammonia. This salt was first noticed by Retzius. It is almost as insoluble in water as bitartrate of potash. Hence, when to a concentrated ammoniacal solution an excess of tartaric acid is added, almost the whole alkali becomes solid.
- 45. Vinate of ammonia. This salt, according to John, crystallizes in needle-form crystals, consisting of rhomboidal prisms. They are transparent, but effloresce when exposed to the air.
- 46. Pyrotartrate of ammonia crystallizes, according to Rose, in plates.
- 47. Citrate of ammonia. This salt, formed by dissolving carbonate of ammonia in citric acid, does not crystallize till its solution be evaporated to the consistency of a thick syrup. Its crystals are elongated prisms. It is very soluble in water. Its taste is cooling and moderately saline. The ammonia is separated by the application of heat.

<sup>\*</sup> Poggendorf's Annalen, vii. 335. † Wöhler, ibid. 331. † Beitrage, iii. 131. © Dobson. | Scheele.

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- 49. Malate of ammonia. This salt is very soluble in water, and does not crystallize.
- 50. Bimalate of ammonia. It forms crystals not altered by exposure to the air, and insoluble in alcohol, as is evident from the experiments of Donovan.
- 51. Fungate of ammonia. This salt probably in the state of bifungate, crystallizes in six-sided prisms, with two of the opposite faces much larger than the rest, and terminating in two faces set on the large faces of the prism, and by meeting, terminating like the roof of a house. It is soluble in twice its weight of cold water.\*
- 52. Mucate of ammonia. Formed by digesting mucic acid in a solution of ammonia. When evaporated, a saline crust remains, having a salt taste. When heated, ammonia is first given off, then the mucic acid undergoes decomposition.
- 53. Pyromucate of ammonia. When the neutral solution is concentrated by evaporation, it gives out half of its ammonia, and is converted into bipyromucate of ammonia, which crystallizes.‡
- 54. Succinate of ammonia. This salt is easily formed by saturating succinic acid with carbonate of ammonia, and concentrating the filtered solution. The crystals are oblique rhombic prisms, the faces of which are inclined at angles of 100° 15′. The inclination of the base of the prism, to one of the contiguous faces is 91° 53′, to the other 93° 25′. The acute lateral edges of the prism are often replaced by tangent planes. So are the alternate terminal edges.§ It has a sharp, bitter, and cooling taste; when exposed to heat, it sublimes without decomposition. It deliquesces when exposed to the air. Its constituents I consider as

1 atom succinic ac	eid	•	•	6.25
l atom ammonia	•	•	•	$2 \cdot 125$
2 atoms water	•	.•	•	2.25

10.625

- 55. Benzoate of ammonia. This salt is easily formed by saturating benzoic acid mixed with water, with carbonate of ammonia. When the solution is sufficiently concentrated, (taking care to add ammonia as it is disengaged,) it deposites crys-
  - \* Braconnot, Ann. de Chim. lxxix. 293.
  - + Scheele and Tromsdorf.
  - † Labillardierc. § Brooke, Annals of Philosophy (2d series), vi. 286.

tals in square plates with bevelled edges, seemingly octahedrons, with their apices deeply truncated. These crystals have a cooling and urinous taste, and leave an impression in the mouth like that of benzoic acid. They undergo no change when exposed to the air. Their specific gravity is 1.414. One part dissolves easily in three parts of hot-water, but a great portion

					18.25
1	atom	water	ۥ	•	1.125
1	atom	ammonia	•	•	$2 \cdot 125$
l	atom	benzoic acid	•'	•	15

is deposited in crystals as the solution cools. Its constituents are

- 56. Bibenzoate of ammonia. When the preceding salt is left exposed to the air, it gradually parts with half of its ammonia, and becomes bibenzoate, which crystallizes in feather-shaped crystals, very little soluble in water, and still less in absolute alcohol.
- 57. Gallate of ammonia. Gallic acid was dissolved in water, and the solution being mixed with an excess of carbonate of ammonia, was placed over sulphuric acid in the vacuum of an air-pump, to get rid of the excess of water and ammonia. After the evaporation a yellowish-gray salt remained, which became green or brown when exposed to the air.\*
- 58. Meconate of ammonia. This salt may be obtained by mixing together two parts of sal ammoniac and three parts of meconate of barytes, and applying heat. The meconate of ammonia sublimes. It crystallizes, according to John, in foursided prisms, which are transparent, and not altered by exposure to the air. They dissolve in 11 times their weight of water. When the crystals obtained from solution in water are heated, they lose water, and then the salt sublimes. According to Choulant this salt is composed of

Meconic ac	cid	•	•	40
Ammonia	•	•	•	42
Water	•	•	•	18

100+

- 59. Boletate of ammonia. It crystallizes in four-sided prisms, not altered by exposure to the air. Taste saline, and somewhat sour. When heated it melts and may be sublimed. ‡ 60. Kinate of ammonia. When the saturated solution of

Berzelius. † Gilbert's Annalen, lvi. 349.

<sup>#</sup> Braconnot.

kinic acid by ammonia is evaporated, it loses half its ammonia, and in that state cannot be regularly crystallized.\*

61. Camphorate of ammonia. This salt crystallizes in fine needles, which become moist by exposure to the air. The taste is sharp and saline. It is soluble in three times its weight of boiling water; but less soluble in cold water. It is soluble likewise in absolute alcohol. When heated it melts, gives out ammonia, and is decomposed, leaving a quantity of charcoal.

When the solution of it in water is boiled, it gives out half its ammonia, and is converted into bicamphorate of ammonia.

- 62. Suberate of ammonia. This salt may be formed by saturating suberic acid by carbonate of ammonia, and then subjecting the solution to spontaneous evaporation. Brandes, by this process obtained it crystallized in needles, and in silky, white, four-sided prisms. It has a sharp saline taste, and is very soluble in water. When heated it melts, and is afterwards decomposed.‡
- 63. Stearate of ammonia. This salt may be formed in the following manner: Put into a narrow and bent glass tube four grains of hydrated stearic acid and fuse it. After it has become solid, fill the tube with mercury, and let up into it 1.6 cubic inches of ammoniacal gas. Heat the acid sufficiently to melt it, and then leave the whole to the mutual reaction of the two constituents. The absorption is at first rapid, and it continues even after the acid has become solid. When the absorption is at an end, the process is finished. The absorption continues for about a month, and the quantity of ammonia absorbed amounts to 1.28 cubic inches. The salt is obviously composed of an atom of each constituent. It is white, and without smell, but has an alkaline taste. It may be sublimed in vacuo. distilled in a retort, ammonia is disengaged, water appears, and there sublimes a substearate mixed with empyreumatic oil. dissolves in hot water, at least in ammoniacal water. On cooling a bistearate is deposited in brilliant scales.§
- 64. Margarate of ammonia. Margaric acid acts upon ammoniacal gas precisely as stearic acid, excepting that the absorption is somewhat slower. The quantity of gas absorbed is sensibly the same as by stearic acid. The salt may be formed also by dissolving the acid in liquid ammonia. When heated in vacuo this salt behaves like stearate of ammonia. It dissolves in hot

<sup>\*</sup> Henry and Plisson, Ann. de Chim. et de Phys. xli. 329.

<sup>†</sup> Brandes, Schweigger's Jour. xxxviii. 287. ‡ Ibid. xxxiii. 85.

<sup>§</sup> Chevrcul, sur les corps gras, p. 56.

water, at least if that liquid contain ammonia. The solution on cooling lets fall bimargarate of ammonia in pearly scales. When exposed to the air at 50° it lets a portion of its ammonia escape.\*

65. Oleate of ammonia. When oleic acid is placed in contact with liquid ammonia, a combination takes place immediately. A gelatinous salt is formed, which dissolves completely in water at the temperature of 60°. When boiled, ammonia is disen-

gaged, and the liquid becomes muddy.

- 66. Phocenate of ammonia. When a glass tube, filled with phocenic acid, is let up into ammoniacal gas, crystals are gradually formed without the appearance of any white smoke. The absorption goes on slowly, and the crystals dissolve into a colourless and transparent liquid. It would appear from this that there are two phocenates of ammonia, the one solid and the other liquid.+
- 67. Butyrate of ammonia. Butyric acid acts upon ammoniacal gas precisely as phocenic acid does. Crystals are formed at first, which are finally dissolved into a liquid, which is thick, but transparent and colourless.
- 68. Caproate of ammonia. The action of caproic acid on ammoniacal gas is precisely similar to that of butyric and phocenic acid.§
  - 69. Cholesterate of ammonia. Brownish-yellow, deliquescing.
- 70. Pinate of ammonia. Pinic acid is easily dissolved by the assistance of heat in caustic ammonia. When the solution cools, the pinate of ammonia precipitates in a slimy, thick state. When boiled a portion of the ammonia is disengaged, and by continuing the heat the whole alcohol is driven off, and the pinic acid remains behind.
- 71. Silvate of ammonia. This salt is formed when a solution of sal ammoniac is poured into liquid silvate of potash. Silvate of ammonia precipitates in the state of a white tarry-like hydrate. It dissolves in 200 times its weight of cold water; but is very soluble in alcohol and ether. The alcoholic solution loses by boiling the greater part of its ammonia, and acquires the property of reddening litmus paper. The aqueous solution decomposes the earthy salts.
- 72. Carbazotate of ammonia. This salt forms very long, flat, brilliant crystals, having a light yellow colour, and very soluble

<sup>\*</sup> Chevreul, sur les corps gras, p. 70. + Ibid. p. 114.

<sup>‡</sup> Ibid. p. 133. § Ibid. p. 142.

<sup>||</sup> Unverdorben, Poggendorf's Annalen, xi. 231.

in water. When heated in a glass tube they melt, and are volatilized without decomposition. When suddenly heated this salt catches fire, and burns quietly, leaving a great quantity of charcoal unconsumed.\*

- 73. Indigotate of ammonia. This salt crystallizes in very long six-sided prisms, transparent, and having the yellow colour of wine. It contains no water of crystallization, and may be sublimed without decomposition.+
- 74. Urate of ammonia. This salt can only be obtained in the state of a white powder. It is pretty soluble in hot, but very sparingly soluble in cold water. Dr. Prout has rendered it probable that it is in the state of urate of ammonia, that uric acid exists in urine. It sometimes constitutes urinary calculi. They have much the appearance of clay, occur most commonly in the bladders of very young persons, and their presence is indicated by an uncommon degree of excitability in the patient, so much so that the least noise or disturbance throws him into a state approaching convulsions. I have seen this species of calculus extracted from four or five children not older than four
- 75. Sulphorinate of ammonia. This salt is very soluble in water, and crystallizes partly in cubes, partly in octahedrons.;
- 76. Xanthate of ammonia. This salt may be formed by saturating xanthic acid with carbonate of ammonia. It may be sublimed without alteration, and is very soluble in water.§
- 77. Sulphonaphthalate of ammonia. Sulphonaphthalic acid forms with ammonia a salt imperfectly crystalline, not deliquescent, but drying when exposed to the air. Taste saline and cooling. It dissolves readily in water and alcohol. When heated on platinum foil it melts, becomes black, burns with flame, and leaves a carbonaceous acid sulphate of ammonia, which by farther heat is entirely dissipated. When its solution is evaporated, it is converted into bisulphonaphthalate of ammonia.

Ammonia enters into the composition of many double salts. The most important of these will be given at the end of this description of the simple oxygen salts.

## SECTION II. -- OF SALTS OF POTASH.

1. The salts of potash, a very few excepted, are soluble in Characters of potash salts.

† Ibid. xli. 178.

\* Ann. de Chim. et de Phys. xxxv. 81. 1 Vogel, Ann. de Chim. et de Phys. xiii. 66.

§ Zeise, Schweigger's Jour. xli. 172.

|| Faraday, Annals of Philosophy (2d series), xii. 207.

II.

water. But in general they are less soluble than those of ammonia.

- 2. Many of them can be obtained in the state of crystals but many of them likewise refuse to crystallize. In general the salts of potash have a less tendency to form regular crystals than the salts of soda.
  - 3. If tartaric acid, dissolved in water, be dropped into an aqueous solution of a salt of potash, the liquid speedily deposites a white granular sediment. This sediment has a sour taste, and consists of small crystals of cream of tartar.
  - 4. If a solution of sulphate of alumina be dropped into a salt of potash, octahedral crystals of alum are very soon deposited.
  - 5. The salts of potash may be exposed to a red heat without being volatilized like the salts of ammonia. If the acid contained in the salt be combustible, it is decomposed, and carbonate of potash, mixed with a little charcoal, remains behind. If the acid is not combustible the salt usually fuses and its nature is not altered: though to this there are some exceptions. Thus the nitric acid is gradually decomposed at a red heat, sulphurous acid lets sulphur sublime, and is converted into sulphuric acid, phosphorous acid allows phosphuretted hydrogen to escape, and is converted into phosphoric acid.
  - 6. The salts of potash are not precipitated by infusion of nutgalls nor by prussiate of potash.
  - 7. They are not affected by sulphuretted hydrogen gas, or by the addition of a hydrosulphuret, except when their acid has a metal for its basis. In which case the acid may be decomposed and precipitated, and the potash left behind.
  - 8. When a solution of platinum is dropped into a salt of potash, an orange-coloured precipitate appears.

Sulphate of alumina and muriate of platinum are precipitated also by salts of ammonia. We must, therefore, in order to know whether a salt so precipitated, contains ammonia or potash for its base, expose it to a red heat. If it be an ammoniacal salt it will be dissipated or decomposed, leaving the acid. But a potash salt will either not be altered, or it will leave carbonate of potash behind.

A salt with base of potash may be distinguished by the blow-pipe in the following manner: Fuse before the blow-pipe a little borax, to which a small portion of oxide of nickel has been added. A yellowish glass is obtained. Fuse this bead with a little of the salt under examination: if it contain potash the bead will assume a bluish colour.

Sp. 1. Sulphate of potash. This salt was known at a very early period of the history of the science, and a great variety of names are given to it, according to the manner of forming it, or the fancy of the operator. Some of these names were, specificum purgans, nitrum fixum, arcanum duplicatum, panacea holsatica, sal de duobus, sal polychrest glaseri, &c.; but it was commonly known by the name of vitriolated tartar, till the French chemists called it sulphate of potash, when they formed their new nomenclature in 1787.\*

Sulphate of potash, or perhaps the bisulphate, was discovered by examining what remained in the retort after the preparation of nitric acid, by distilling a mixture of sulphuric acid and nitre. It was the salt obtained from this residuum that was called panacea duplicata or arcanum duplicatum. The Duke of Holstein, sometime before the year 1663, purchased the preparation of this salt for 500 dollars as a remedy in fevers, stone, and scurvy.

Sulphate of potash is easily procured by saturating the acid salt (which remains after the preparation of nitric acid) with potash, and setting it aside to crystallize. The primary form crystal of the crystal is a right rhombic prism, the faces of which meet at angles of 120° 30′. Most commonly two of the opposite lateral edges are replaced by tangent planes, converting the crystals into a six-sided prism. The edges of the base of the prism are also replaced by planes, which convert the end of the prism into a pyramid, either complete or wanting the apex.

The figure in the margin represents the most usual shape. P, M and M' are the faces of the primary figure, h the face formed by replacing one of the lateral edges, and c, e,  $\acute{e}$  the pyramidal faces made by replacing the terminal edges. The measurements of these faces, made by Mr. W. Phillips, are as follows.

M on M'	•	•	120° 30′
M on h	•	•	120 45
M on e	•	•	146 22
h on $c$	•	•	146 10
c on e		_	13 12

<sup>\*</sup> Bergman called it alkali vegetabile vitriolatum, and Morveau vitriol of potash.

<sup>†</sup> Shaw's Boyle, i. 64.

Not uncommonly three of the crystals are aggregated together so as to constitute a macle.\*

Sulphate of potash has a very disagreeable bitter taste. Its specific gravity, according to Wallerius,† is 2.298; according to Hassenfratz, 2.4073;‡ according to Watson, 2.636.§ I found it 2.66. At the temperature of 60° it dissolves in 16 times its weight of water: in a boiling heat it is soluble in five times its weight. When it is boiled in water, that liquid dissolves 0.242 parts, or nearly ¼th of its weight of it.¶

It suffers no alteration when exposed to the air. When placed upon burning coals, it decrepitates, but suffers no other alteration. In a red heat it melts. It is sometimes luminous in the dark, as Mr. Giobert has observed.\*\* It contains no water of crystallization, and is composed of

1 atom sulphuric	acid	•	•	5
1 atom potash	•	•	•	6
				11

2. Sesquisulphate of potash. This salt was obtained by Mr. Phillips while evaporating, the residual salt remaining after distilling a mixture of equal weights of nitre and sulphuric acid. It is a white salt which crystallizes in long slender needles like asbestus. Its taste is sour and bitter, and its constituents, according to the analysis of Mr. Phillips, are

Sulphuric	acid	•	•	$52 \cdot 45$
Potash	•	•	•	42.80
$\mathbf{W}$ ater	•	•	•	4.75
				100.00

This is obviously

1 atom sulphuric	acid	•	•	<b>7·5</b>
l atom potash	•	•	•	6
$\frac{1}{2}$ atom water	•	•	. •	0.5625

14.0625++

- 3. Bisulphate of potash. This salt is obtained when we mix sulphate of potash with half its weight of sulphuric acid, and
- \* See an account of the crystals of this salt in Annals of Philosophy (new series), iv. 342.
  - † Chemistry, p. 265.
  - § Chemical Essays, v. 67.
  - ¶ Wenzel's Verwandschaft, p. 310.
- †† Phil. Mag. (2d series), ii. 249.
- ‡ Ann. de Chim. xxviii. 12.
- || Bergman, i. 135.
- \*\* Ann. de Chim. x. 40.

expose the mixture to incipient redness in a platinum crucible till it ceases to lose acid. When dissolved in water, and set aside it crystallizes in thin rhomboidal plates, the plane angles of the large faces of which are 97° 20' and 82° 40', and the faces of the prism are inclined to each other at angles of 107° 15'. Its taste is very acid and sharp. It melts easily when heated, and flows like an oil. A very strong heat is necessary to drive off the excess of acid, unless we neutralize it by means of ammonia. It dissolves in about twice its weight of cold, and in less than its weight of boiling water. When alcohol is poured into the solution, sulphate of potash precipitates. When exposed to the air it effloresces slightly. The composition of this salt was first accurately determined by Dr. Wollaston.\*\* It is a compound of

2 atoms sulphuric	acid		•	10
1 atom potash	•	•	•	6
2 atoms water	•	•	•	2.25
				18.25+

4. Sulphite of potash. This salt may be obtained by passing a current of sulphurous acid gas through a solution of potash till the alkali be saturated. Its crystals are white and transparent: their figure that of rhomboidal plates. Its crystallization often presents small needles diverging from a common centre.‡ Its specific gravity is 1.586.§ Its taste is penetrating and sulphureous. At the common temperature of the atmosphere it is soluble in its own weight of water, but much more soluble in boiling water. When exposed to the air, it scarcely changes its appearance, loses about 2 per cent. of its weight, and then is gradually, but very slowly, converted into sulphate of potash. When exposed to a sudden heat, it decrepitates, loses its water, and a portion of its acid; then a quantity of sulphur is disengaged from the remaining acid, and the residuum is sulphate of potash, with a slight excess of alkali. Nitric acid converts it into sulphate of potash by imparting oxygen. So does chlorine, but imperfectly, as it drives off a portion of its acid unchanged.

It seems to contain no water of crystallization, but to be a compound of

<sup>\*</sup> Phil. Trans. 1808, p. 96. † First Principles, ii. 254.

<sup>‡</sup> Fourcroy and Vauquelin, Nicholson's Journal, i. 317.

<sup>§</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

Class I,

5. Bisulphite of potash. This salt is easily obtained by adding an additional dose of sulphurous acid to the last salt. It crystallizes more readily than sulphite, but has not been particularly examined.

6. Hyposulphite of potash. This salt is easily formed by exposing hydroguretted sulphuret of potash to the atmosphere till it loses its yellow colour. The liquid is then a solution of hyposulphite of potash. When sufficiently concentrated it crystallizes in a confused mass of spiculæ. The crystals are long rectangular four-sided prisms with square bases. It has a penetrating taste like nitre, succeeded by a bitterness, and is very deliquescent. The deliquiated salt crystallizes in fine needles by a slight diminution of temperature. By the action

When a saturated solution of sulphuret of potassium in alcohol is set aside in an uncorked phial, beautiful crystals of this salt are gradually deposited.+

of a graduated heat it boils down to a dry white mass, then takes fire and burns much like a piece of tinder, but with a weak blue flame. It dissolves chloride of silver, even when

7. Hyposulphate of potash. This salt crystallizes in cylindroidal prisms, terminated by a plane perpendicular to their axis; tor in dodecahedrons composed of two six-sided pyramids, applied base to base. The figure of the crystal is very minutely described by M. Heeren. It dissolves in 1.58 parts of boiling and in 16.5 parts of cold water. It contains no water of crystallization; but is composed of

History.

8. Nitrate of potash. As this salt, known also by the name of saltpetre, is produced naturally in considerable quantities, particularly in Egypt, it is highly probable that the ancients were acquainted with it: but scarcely any thing certain can be collected from their writings. If Pliny mentions it at all,

very dilute, with great readiness.\*

<sup>\*</sup> Herschell; Edin. Phil. Jour. i. 19.

<sup>• ‡</sup> Annals of Philosophy, xiv. 355.

<sup>|</sup> Heeren, Ibid. p. 76.

<sup>†</sup> Berzelius.

<sup>§</sup> Poggendorf's Annalen, vii. 73.

he confounds it with carbonate of soda, which was known by the name of nitron and nitrum. It is certain, however, that it has been known in the East from time immemorial. Roger Bacon mentions this salt in the 13th century under the name of nitre. The word nitre (nitrum) was applied by the ancients to carbonate of soda. When nitrate of potash was first observed it probably got the same name, from the supposition that it was the same kind of salt. After the difference became known the term nitre was naturally applied, exclusively to the most important of the two, which is unquestionably saltpetre.

No phenomenon has excited the attention of chemical philosophers more than the continual reproduction of nitre in certain places after it had been extracted from them. Prodigious quantities of this salt are necessary for the purposes of war; and as nature has not laid up great magazines of it, as she has of some other salts, this annual reproduction is the only source from which it can be procured. It became, therefore, of the utmost consequence, if possible, to discover the means which nature employed in forming it, in order to enable us to imitate her processes by art, or at least to accelerate and facilitate them at pleasure. Numerous attempts accordingly have been made to explain and to imitate these processes.

Stahl, setting out on the principle that there is only one acid in nature, supposed that nitric acid is merely sulphuric acid combined with phlogiston, and that this combination is produced by putrefaction; he affirmed, accordingly, that nitre is composed by uniting together potash, sulphuric acid, and phlogiston. But this opinion, which was merely supported by very far-fetched analogies, could not stand the test of a rigorous examination.

Lemery, the younger, accordingly advanced another, affirming, that all the nitre obtained exists previously in animals and vegetables, and that it is formed in these substances by the processes of vegetation and animalization. But it was soon discovered that nitre exists, and is actually formed, in many places where no animal nor vegetable substance had been decomposed: and consequently this theory was as untenable as the former. So far indeed is it from being true, that nitre is formed by these processes alone, that the quantity of nitre in plants has been found to depend entirely on the soil in which they grow.\*

At last, by the numerous experiments of several French Bouillon.

philosophers, particularly by those of Thouvenel, it was discovered that nothing else is necessary for the production of nitre but a basis of lime, heat, and an open, but not too free communication with dry atmospheric air. When these circumstances combine, the acid is first formed, and afterwards the alkali makes its appearance. How the air furnishes materials for this production is easily explained, now that the component parts of the nitric acid are, known to be oxygen and azote: but how lime contributes to their union it is not so easy to see. The appearance of the potash is equally extraordinary.

Nitre is found abundantly on the surface of the earth in India, South Africa, and even in some parts of Spain. In Germany and France it is obtained by means of artificial nitre beds. These consist of the refuse of animal and vegetable bodies undergoing putrefaction, mixed with calcareous and other earths. It has been ascertained, that if oxygen gas be presented to azote at the instant of its disengagement, nitric acid is formed. This seems to explain the origin of the acid in these beds. The azote disengaged from these putrefying animal substances combines with the oxygen of the air. The potash is probably furnished, partly, at least, by the vegetables and the soil.

The nitre is extracted from these beds by lixiviating the earthy matters with water. This water, when sufficiently impregnated, is evaporated, and a brown-coloured salt obtained, known by the name of *crude nitre*. It consists of nitre, common salt, nitrate of lime, and various other salts. The foreign salts are either separated by repeated crystallizations, or by washing the salt repeatedly with small quantities of water; for the foreign salts being more soluble are taken up first.

Crystal.

Nitre, when slowly evaporated, is obtained in six-sided prisms, terminated by six-sided pyramids; but for most purposes it is preferred in an irregular mass, because in that state it contains less water. The primitive form of its crystals, according to Haiiy, is a rectangular octahedron, composed of two four-sided pyramids applied base to base; two of the sides are inclined to the other pyramid at the angle of 120; the other two at an angle of 111°. The six-sided prism is the most common form which it assumes. Sometimes, instead of six-sided pyramids, these prisms are terminated by 18 facets, disposed in three ranges of six, as if three truncated pyramids were piled on each other; sometimes it crystallizes in tables.\*

<sup>\*</sup> Traité de Mineralogie, ii. 346.

The specific gravity of nitre, as ascertained by Dr. Watson, is 1.933.\* Its taste is sharp, bitterish, and cooling. It is very brittle.

100 parts of water at 32° dissolve 13.32 of this salt.

t	41°.018, 10	0 water dissolve	16.72 parts
	<b>53</b>		$22 \cdot 23$
	$64\frac{1}{4}$		29.31
	76.9		38.40
	95 i		<b>54</b> ·82
	113		74.66
	$130^{\circ}_{o}$ .		97.05
	149.8		125.42
	$175\frac{1}{2}$		169-27
	207.8	•	236·45†

Alcohol, of the specific gravity 878, dissolves  $\frac{1}{100}$ th of its weight of this salt, but stronger alcohol takes up no sensible portion of it. 1 it is not altered by exposure to the air.

When the solution of nitre is exposed to a boiling heat, part of the salt is evaporated along with the water, as Wallerius, Kirwan, and Lavoisier observed successively. When exposed to a strong heat it melts, and congeals by cooling into an opaque mass, which has been called *mineral crystal*. When heated nearly to redness it begins to disengage oxygen; and by keeping it in a red heat, about the third of its weight of that gas may be obtained; towards the end of the process azotic gas is disengaged. If the heat be continued long enough, the salt is completely decomposed, and pure potash remains behind. When simply brought into fusion, and then allowed to cool, it assumes a radiated texture. The broader these radii are the purer is the salt. A mixture of about  $\frac{1}{30}$ th of common salt completely destroys the radiated appearance.

It detonates more violently with combustible bodies than any of the other nitrates. When mixed with one-third part of its weight of charcoal, and thrown into a red-hot crucible, or when charcoal is thrown into red-hot nitre, detonation takes place, and one of the most brilliant combustions that can be exhibited. The residuum is carbonate of potash. It was formerly called nitre fixed by charcoal. The alchymists performed this experiment in a tubulated earthen retort, to which an

<sup>\*</sup> Essays, v. 67. Wallerius makes it 1.900 (Chemistry, p. 266); Hassenfratz found it 1.9369 (Ann. de Chim. xxviii. 12.); Fahrenheit had stated it as long ago as 1724 at 2.150 (Phil. Trans. xxxiii. 114); I found it 2.4.

<sup>†</sup> Gay-Lussac; Annals of Philosophy, xv. 11. 

\*Kirwan.

apparatus of glass vessels was luted. After every portion of nitre and charcoal which they threw in, they shut up the retort. The carbonic acid and azotic gas which were disengaged often burst their apparatus. To the small quantity of water which they obtained in their vessels, they gave the name of clyssus, and ascribed to it a great many virtues. A still more violent detonation is produced by using phosphorus instead of charcoal. When a mixture of nitre and phosphorus is struck smartly with a hot hammer, a very violent detonation is produced.\*

Fulminating

When three parts of nitre, two parts of dry potash, and one part of sulphur are triturated together in a mortar, a powder is formed, which was known more than a century ago, and distinguished by the name of fulminating powder. When heated gradually till it enters into fusion, it takes fire suddenly and burns with a violent explosion. By the fusion sulphuret of potassium is formed, which being intimately mixed with the nitre, and the heat by the fusion being rendered equable throughout the mass, the whole burns at the same instant. Hence the reason of the violence of the explosion.

Nitre contains no water of crystallization, but there are often cavities in which that liquid is mechanically lodged. Supposing it pure its constituents are

1 atom nitric acid	•	•	6.75
l atom potash .	•	•	6
			12.75

Nitre furnishes all the nitric acid in all its states employed either by chemists or artists. When burnt with tartar it yields a pure carbonate of potash. In the assaying of various ores it is indispensable, and is equally necessary in the analysis of many vegetable and animal substances. But one of the most important compounds formed by means of nitre is gunpowder, which has completely changed the modern art of war. The discoverer of this compound, and the person who first thought of applying it to the purposes of war are unknown. It is certain, however, that it was used in the 14th century. From certain archives quoted by Wiegleb, it appears that cannons were employed in Germany before the year 1372. No traces of it can be found in any European author previous to the 13th century; but it seems to have been known to the Chinese long before that period. There is reason to believe that cannons were used in the battle of Cressy, which was fought in

Gunpowder.

<sup>\*</sup> Brugnatelli; Ann. de Chim. xxvii. 74.

1346. They seem even to have been used three years earlier at the siege of Algesiras; but before this time they must have been known in Germany, as there is a piece of ordnance at Amberg, on which is inscribed the year 1303. Roger Bacon, who died in 1292, knew the properties of gunpowder; but it does not follow that he was acquainted with its application to fire-arms.\*

Sect. 11.

Gunpowder is composed of nitre, sulphur, and charcoal, composition. reduced to powder, and mixed intimately with each other. The proportion of the ingredients varies very considerably; but good gunpowder may be composed of the following proportions.

76 parts nitre15 charcoal9 sulphur

100

These ingredients are first reduced to a fine powder, separately, then mixed intimately, and formed into a thick paste with water. After this has dried a little, it is placed upon a kind of sieve full of small holes, through which it is forced. By that process it is divided into grains, the size of which depends upon the size of the holes through which they have been squeezed. The powder, when dry, is put into barrels, which are made to turn round on their axes. By this motion the grains of gunpowder rub against each other, their asperities are worn off, and their surfaces are made smooth. The powder is then said to be glazed.

Gunpowder, as is well known, explodes violently when a properties. red heat is applied to it. This combustion takes place even in a vacuum; a vast quantity of gas is emitted, the sudden production of which is the cause of all the violent effects which this substance produces. The combustion is evidently owing to the decomposition of the nitre by the charcoal and sulphur. The products are carbonic acid gas, azotic gas, sulphurous acid gas, and probably sulphuretted hydrogen. Mr. Cruickshanks has ascertained that no perceptible quantity of water is formed. What remains after the combustion is potash combined with a small portion of carbonic acid, sulphate of

\* See Watson's Chemical Essays, Vol. i. 327, for a full detail of the facts respecting this subject. From Barbour's Life of Robert Bruce, it appears that guns were used by the English for the first time about the year 1320.

+ For a full detail of every thing respecting the proportions and manufacture of gunpowder, the reader is referred to a very interesting dissertation by Dr. Watson, Essays, ii. I, and to Baumé's Chemistry, i. 455.

potash, a very small proportion of sulphuret of potassium, and unconsumed charcoal.\* This mixture soon attracts moisture, and the sulphuret which it contains enables it to act strongly on metallic bodies.

A mixture of equal parts of tartar and nitre, deflagrated in a crucible, is known by the name of white flux. It is merely a mixture of carbonate of potash with some pure potash. When two parts of tartar and one of nitre are deflagrated in this manner, the residuum is called black flux from its colour. It is merely a mixture of charcoal and carbonate of potash.

9. Hyponitrite of potash. This salt may be obtained by decomposing hyponitrite of lead by carbonate of potash, or by keeping nitre in fusion till the disengagement of oxygen gas without any augmentation of temperature ceases. The salt is then allowed to cool and dissolved in water. The first crystals that are deposited are usually of nitrate of potash; then the hyponitrite makes its appearance. This salt contains no water of crystallization, but is composed of

1 atom hyponitrous acid . 4.75
1 atom potash . . . 6

10. Chlorate of potash. This salt was discovered by Berthollet,+ and has been very much investigated by chemists in general.

It is prepared by dissolving one part of carbonate of potash in six parts of water, putting the mixture into a Woolfe's bottle, and saturating the potash with chlorine gas.‡ When the saturation is nearly completed, the chlorate falls down in crystals. It may be purified by solution in boiling water. As the water cools, the pure chlorate crystallizes. The crystals are to be dried between folds of blotting paper.

According to Haiiy, the primitive form of the crystals of chlorate of potash is an obtuse rhomboidal prism; but it is usually obtained in small thin plates of a silvery whiteness. It is only by allowing an unsaturated solution of it in boiling

<sup>\*</sup> Cruickshanks, Nicholson's Journal, iv. 258.

<sup>†</sup> It was, in fact, first discovered by Dr. Higgins, who mentions it in 1786; but appears to have mistaken it for nitre. See Higgins on Acetous Acid, &c. p. 180.

<sup>‡</sup> The bottle containing the alkali must be covered up from the light, otherwise no crystals of chlorate can be obtained, as I have more than once experienced.

water to cool slowly, or by exposing a solution in cold water to spontaneous evaporation, that it is obtained in large regular rhomboidal crystals.

Its taste is cooling, austere, and disagreeable, somewhat analogous to that of nitre. Its specific gravity is 1.989.\* Its solubility in water, as determined by Gay-Lussac, is as follows:

100 water dissolves	3.33 of the salt
	5.6
	6.03
	8.44
	12.05
	18.96
	35.40
	60·24†

It is not sensibly altered by exposure to the air. If the heat be raised to redness, it rapidly gives out more than the third of its weight of oxygen gas. It is from this salt that oxygen gas can be obtained in the state of the greatest purity. the effervescence is over, there remains common chloride of potassium.

The most astonishing of its properties are those which it exhibits when mixed with combustibles. All combustible substances whatever are capable of decomposing it, and in general the decomposition is attended with violent detonations.

When three parts of this salt and one part of sulphur are recussion triturated in a mortar, the mixture detonates violently: the powder. same effect is produced when the mixture is placed upon an anvil and struck smartly with a hammer. Nay, it even sometimes detonates spontaneously without any perceptible friction, and ought not therefore to be kept ready mixed. Charcoal produces the same effects, though not so violent. This property induced Berthollet to propose it as a substitute for nitre in the preparation of gunpowder. The attempt was made at Essone in 1788; but no sooner had the workmen begun to triturate the mixture of charcoal, sulphur, and chlorate, than it exploded with violence, and proved fatal to Mr. Letors and Mademoiselle Chevraud. The force of this gunpowder when it is prepared, is greater than that of the common sort of powder; but the danger of preparing it, and even of using it after

<sup>\*</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

<sup>+</sup> Annals of Philosophy, xv. 11.

it is prepared, is so great, that it can hardly ever be substituted with advantage for common gunpowder.

Phosphorus also detonates with this salt either by trituration or percussion. The quantities of each used ought not to exceed half a grain, or at most a grain, otherwise the experiment may be attended with some danger. It detonates also when treated in the same way with almost all the metals, and likewise with cinnabar, pyrites, sugar, gums, oils, alcohol, &c. When thrown upon platinum heated to whiteness, it does not detonate but The surface of the platinum, however, is oxidized; for acetic acid dissolves a part of it; and when prussiate of lime is poured into the solution, the liquid becomes of a greenish white colour.\* When this salt is triturated in a mortar with a little cotton cloth, small repeated explosions are heard, similar to the crack of a whip, and if the cotton be dry and warm it sometimes takes fire. It always does so when, after the trituration has been continued for some time, sulphuric acid is poured upon the cotton. When nitric acid is poured upon a mixture of chlorate of potash and phosphorus, flakes of fire are emitted at intervals for a considerable time.+

The theory of these explosions was first pointed out by Berthollet. The oxygen of the acid combines with the combustible, and at the same time lets go a quantity of caloric; and trituration or percussion acts merely by bringing the particles which combine within the sphere of each other's attraction.

When this salt is heated to incipient ignition it gives out oxygen gas in abundance, and chloride of potassium remains. In this way it has been analyzed, and shown to be a compound of

1 atom chloric acid		•	9.5
1 atom potash .	•	•	6
			3

15.5

Matches.

Advantage has been taken of the properties of this salt to make matches, which take fire when dipped into sulphuric acid. Thirty parts of the salt in fine powder are intimately mixed with ten parts of levigated sulphur, 8 parts of sugar, 5 of gum arabic, and a sufficient quantity of cinnabar, to give the whole a red colour. The sugar, gum, and salt, are first mixed intimately, then water enough is added to bring the whole to the consistence of thick cream. Lastly, the sulphur is added,

<sup>\*</sup> Morveau, Ann. de Chim. xxv, 18. + Collier, Manchester Mem. v. 229.

and the whole well kneaded together. Matches already coated seed. 11. with sulphur are dipped into this matter, and thus coated over with a thin crust of the mixture and allowed to dry. When these matches are dipped into sulphuric acid they kindle and set fire to the sulphur, and thus may be employed to light a candle.

What is called percussion powder, is merely a gunpowder in which chlorate of potash is substituted for nitre. A little of it is put into a thin copper thimble. When struck it catches fire and explodes the powder in the piece.

11. Bromate of potash. This salt is obtained when bromine is dissolved in caustic potash ley. It precipitates as it forms in the state of a white powder. It is little soluble in cold water, but much more soluble in boiling water, and as the solution cools it is deposited in needles or crystalline plates. When heated it behaves like chlorate of potash.\* It has not been rigorously analyzed, but from the experiments of Balard there can be little doubt that it is a compound of

1 atom bromic acid	•	•	15
1 atom potash .	•	•	6
			21

12. Iodate of potash. The easiest mode of forming this salt is to pass a current of chlorine gas through iodine till a combination is formed, which is to be saturated with caustic potash. Iodate of potash precipitates, while chloride of potassium remains in solution. The iodate is to be dissolved in boiling water and set aside to crystallize. Its crystals are so small that their figure has not hitherto been ascertained. This salt is not altered by exposure to the air. One hundred parts of water at 57° dissolve 7.43 parts of this salt. When heated to redness, oxygen gas is disengaged and iodide of potassium remains: on burning coals it fuses and deflagrates like nitre.+ 1 part of this salt at 57° dissolves in 13.45 parts of water. is insoluble in alcohol. Sulphuric acid dissolves it when assisted by heat, without decomposing it. 100 parts of this salt when heated to redness give out about 22½ of oxygen gas. The constituents are

<sup>\*</sup> Balard, Ann. de Chim. et de Phys. xxxii. 365.

<sup>+</sup> Gay-Lussac, Ann. de Chim. xci. 74.

1 atom iodic acid	•	•	20.75
1 atom potash	•	•	6
			00 ==

26.75

There exists a disiodate of potash which crystallizes, but has not been hitherto accurately examined.

13. Carbonate of potash. This salt has been long known to chemists; and before its composition was ascertained by Black, it was characterized by a great variety of names, according to the manner of preparing it; such as fixed nitre, salt of tartar, vegetable alkali, &c. Its properties were first described with precision by Bergman in 1774.\*

The pearl ash of commerce is a carbonate, but very much mixed with foreign substances. It may be freed from the greater number of these foreign bodies by pouring on it its own weight of water and allowing the whole to remain for 24 hours under occasional agitation. The water is then decanted off and evaporated to dryness. Most of the foreign salts remain undissolved. The salt thus purified is sold by apothecaries under the name of salt of tartar. It is still too impure for chemical purposes. Pure carbonate of potash may be obtained by heating bicarbonate of potash, or by burning pure cream of tartar or a mixture of equal parts of cream of tartar and nitre, and dissolving the residue in water and evaporating the solution. When the solution is concentrated till its specific gravity is 1.62, and then put into a tall cylindrical glass vessel and left to cool slowly, it deposites crystals which have the form of rhomboidal plates, and which speedily deliquesce when exposed to the air.+ The primary form of the crystal is an octahedron with a rhombic base, the angles of the rhomb are 122° and 58°.

Carbonate of potash, thus obtained, is a white salt having a strong alkaline taste, but not caustic. It changes vegetable blues to green, and deliquesces rapidly when exposed to the air. It is insoluble in alcohol, but very soluble in water. It is composed of

1 ator	n carbonic	acid	•	•	2.75
1 aton	n potash	•	• •	•	6
2 aton	ns water	•	•	•	2.25

<sup>11</sup> 

<sup>\*</sup> Opusc. i. 13.

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The potash of commerce is always in the state of a carbonate; but it contains likewise several foreign substances which render the proportion of alkali variable. Mr. Kirwan has pointed out a very ingenious method of detecting the quantity of alkali in any specimen, by the property which it has of precipitating alumina from alum; and Vauquelin has published a still simpler method, namely, the quantity of nitric acid of a given density necessary to saturate a given weight of the salt. From his experiments, we learn that the following kinds of this salt known in commerce contain the following ingredients:\*

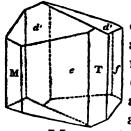
	Potash.	Sulphate of potash.	Muriate of potash.	Insoluble residue.	Carbonic acid and water.	Total,
Potash of Russia	772	65	5	56	254	1152
——— America	857	154	20	2	119	1152
American Pearl-ash	754	80	4	6	308	1152
Potash of Treves .	720	165	44	24	199	1152
——— Dantzic	603	152	14	79	304	1152
Vosges	444	148	510	34	304	1440

Still simpler and more accurate methods of determining the purity of these bodies have been contrived by Decroizille and Gay-Lussac. But it seems scarcely necessary to point out these methods, as the use of potash in this country is diminishing very rapidly, carbonate of soda being gradually taking its place. And this last alkali is prepared by our manufacturers in a state approaching so nearly to purity, that there is seldom occasion for testing it.

14. Bicarbonate of potash. This salt is formed by saturating potash with carbonic acid, which is best done by causing the gas to pass through a solution of potash till it refuses to absorb any more. The potash of commerce is an impure carbonate of potash: by distilling it with solid carbonate of ammonia, it may be converted into bicarbonate of potash. When potash

<sup>\*</sup> Ann. de Chim. xl. 273.

of silica. Mr. Pelletier has proposed this saturation as the best method of purifying potash from the earth.



The primary form of the crystal is a right oblique prism, the faces of which meet at angles of 103° 25′. The figure in the margin represents the most common secondary form (except that the face T is usually wanting), and the following are the measurements of the angles by Mr. Brooke:\*

M on a pla	ne par	allel t	o f		•	127°	35′
M on e	•	•	•	•	•	126	45
T on e	•	•	•	•	•	156	<b>50</b>
T on f		•	•	•	•	128	<b>50</b>
e on f	•	•	•	•	•	105	<b>40</b>
M on d'	•	•	•	•	•	111	00
d' on d'	•	•			•	138	00

This salt has an alkaline, but not a caustic taste, and still gives a green colour to vegetable blues. Its specific gravity is 2.012.+ It is soluble at the common temperature in about four times its weight of water.‡ Boiling water dissolves  $\frac{5}{6}$ ths of its weight.§ Alcohol, even when hot, does not dissolve above  $\frac{1}{1200}$ th part of it. Pelletier has observed, that when the crystallized salt is dissolved in boiling water, bubbles of carbonic acid gas are emitted. It is not altered by exposure to the air. Heat deprives it of its water and part of its acid, but does not decompose it completely.

Dr. Wollaston first demonstrated that this salt contains twice as much carbonic acid as the preceding. The water which it contains amounts to very nearly  $1\frac{1}{2}$  atom; but most probably the excess above one atom is merely lodged between the plates of the crystals. We may therefore consider the salt as composed of

2 atoms carbonic	acid	•	•	<b>5·5</b>
1 atom potash	•	•	•	6
l atom water	. •	•	•	1.125
				12.625

15. Sesquicarbonate of potash. I first got a specimen of this salt from the late Dr. Nimmo of Glasgow, who had obtained

<sup>\*</sup> Annals of Philosophy (2d series) vi. 42.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

<sup>‡</sup> Bergman, i. 13. § Pelletier.

it accidentally without being aware of its nature. Upon analyzing it I ascertained its nature. It is easily obtained by dissolving bicarbonate of potash in water, and boiling the solution. One-fourth of the carbonic acid is expelled, and, of course, a sesquicarbonate remains. The only crystals of it that. I have obtained are irregular six-sided plates. They are translucent, and have nearly the same taste as the bicarbonate. I found them composed of

 $1\frac{1}{2}$  atom carbonic acid...4.1251 atom potash...66 atoms water...6.75

16.875

16. Phosphate of potash. This salt may be obtained by adding carbonate of potash to hot phosphoric acid, till the solution ceases to produce any effect upon vegetable blues. When this solution is sufficiently concentrated, and set aside in a dry place it gradually deposites phosphate of potash in small transparent crystals. These crystals are four-sided prisms terminated by four-sided pyramids. The sides of the prism are all equal, and its angles right angles. Sometimes the intervening prism is wanting so that the crystals have the form of small octahedrons. This salt has a cooling and somewhat urinous taste, but neither strong nor disagreeable. It is not altered by exposure to the air. It is very soluble in water, and melts into a liquid when exposed to a red heat. While in a state of fusion its colour is yellow; but it again assumes its white colour on cooling. I consider it as composed of

1 atom phosphoric	acid	•	•	4.5
l atom potash	•	•	•	6
l atom water	•	•	•	1.125

11.625

But the analysis would require repetition. The crystals of this salt are so difficult to procure, that in most chemical books it is described as uncrystallizable.

17. Biphosphate of potash. This salt is easily obtained by adding carbonate of potash to phosphoric acid, till litmus paper reddened by it resumes its blue colour when dried in the air. The salt shoots into large crystals when the liquid is concentrated to the requisite point. The primary form of the crystal is a right square prism. Two opposite faces of the prism are often much enlarged at the expense of the two others.

The prism is usually terminated by a four-sided pyramid which is most frequently truncated.\* It has a saline and cooling taste, dissolves readily in water; but is insoluble in alcohol. composition, as determined by the experiments of Mitcherlich are

2 atoms phosphoric	acid	•	•	9
1 atom potash	•	•	•	6
2 atoms water	•	• •	•	2.25
				17.25

18. Diphosphate of potash. This salt may be obtained by adding hydrate of potash to a solution of the phosphate, evaporating to dryness, and removing the excess of potash by alcohol. This salt is tasteless and insoluble in cold water, but soluble in hot water; and it precipitates as the solution cools in a gritty powder. It is extremely fusible; melting before the blow-pipe into a transparent bead, which becomes opaque on cooling. It is soluble in nitric, muriatic, and phosphoric acids: the solutions are thick, glutinous, and adhesive. When sufficiently diluted, the alkalies occasion no precipitate in these solutions; but when they are concentrated, a precipitate appears. I consider this as a compound of

I atom phosphoric a	cid	•	•	4.5
2 atoms potash	•	•	•	12
				16.5

A subphosphate of potash, analyzed by Saussure, was found to be a compound of

Phosphoric acid	d f	•	•	$3 \cdot 5$
Potash	•	•	•	6.5
				10.0‡

This approaches

1 atom phosphoric	acid	•	•	4.5
$l_{\frac{1}{2}}$ atom potash	•	•	•	9

13.5

From this it is probable that there are two subphosphates of potash.

19. Phosphite of potash. This salt is incrystallizable, deliquescent, and insoluble in alcohol.§

<sup>\*</sup> See Mitcherlich, Ann. de Chim. et de Phys. xix. 370. + Ibid. p. 364. † Sur la vegetation, p. 321. § Dulong.

Sect. II.

- 20. Hypophosphite of potash. This salt is obtained by boiling phosphorus in a potash ley. It does not crystallize, but forms a saline mass, soluble in alcohol, and deliquescing more rapidly than chloride of calcium. In consequence of its solubility in alcohol, it is easily freed from phosphates or phosphites, when it happens to contain them.\*
- 21. Arseniate of potash. This salt is obtained by neutralizing arsenic acid with potash, and evaporating the solution. We obtain an incrystallizable salt, which deliquesces in the air, renders syrup of violets green, but does not alter the infusion of turnsole. When heated in a clay crucible, it is partly converted into a white glass, and partly changed into arseniate of potash. When mixed with one-eighth of its weight of charcoal powder, and distilled in a retort, it swells and bubbles up violently, evidently in consequence of the disengagement of carbonic acid gas, and at the same time a quantity of arsenic is sublimed: the residuum is merely carbonate of potash and charcoal.

This salt is a compound of 1 atom of arsenic acid and 1 atom of potash. The proportion of water which it contains has not been determined.

22. Binarseniate of potash. This salt was first formed by Macquer; and for that reason was long distinguished by the name of arsenical neutral salt of Macquer. He obtained it by distilling in a retort a mixture, consisting of equal parts of white oxide of arsenic and nitre. After the distillation, the white saline mass, which remained in the retort, was dissolved in hot water and filtered. When properly evaporated, beautiful transparent crystals of binarseniate of potash are obtained.

Scheele first ascertained the composition of this salt, by discovering that it was obtained by adding arsenic acid to the arseniate of potash till the solution ceases to alter the colour of syrup of violets. It then reddens the infusion of turnsole, and yields by evaporation fine crystals of Macquer's neutral salt.

Mitcherlich has shown that the crystals of this salt have the same shape as those of biphosphate of potash,‡ a right square prism, usually terminated by four-sided pyramids, the faces of which are inclined on the corresponding faces of the prism at angles of 133° 12'.§

This salt has a saline and cooling taste, somewhat similar to

<sup>\*</sup> Dulong. † Mem. Par. 1746, p. 223,

<sup>‡</sup> See also Mr. Brooke, Annals of Philosophy, v. 450.

<sup>\$</sup> Ann. de Chim. et de Phys. xix. 370.

that of nitre. It is not altered by exposure to the air. Specific gravity 2.638. It may be kept in a heat of 550° for a considerable time without melting or undergoing any sensible change. In a red heat it melts and becomes as liquid as water. The congealed salt is opaque or only translucent. By this treatment it loses 7.5 per cent. of its weight.

It is insoluble in alcohol. 100 parts of water at the temperature of 42° dissolve 19.047 parts of this salt. The specific gravity of this solution (at 60°) is 1.1134. It is much more soluble in hot than in cold water. Hence a saturated solution in hot water crystallizes very readily on cooling. I found the constituents of this salt

Argania agid

	Arsenic 8	ıcıu	•	•	U	J 420
	Potash	•	•	•	2	7.074
	Water	•	•	•		7.500
					10	0.000*
This is	almost exactly	7				
	2 atoms arse	enic ac	eid	•	•	14.5
	1 atom potas	sh	•	•	•	6
	$l_{\frac{1}{2}}$ atom wate	r	•	•	•	1.6875

22.1875

65.426

But Mitcherlich obtained nearly 10 per cent. of water of crystallization, which would elevate the water to two atoms.† The salt which I analyzed had been in my possession for upwards of 20 years. Whether this might not have diminished the water of crystallization, I cannot say.

- 23. Arsenite of potash. When arsenious acid is dissolved in carbonate of potash to saturation, if we evaporate the solution the acid separates in octahedral crystals. This does not happen when caustic potash is employed. But the solution cannot be crystallized.
- 24. Borate of potash. This salt has been very little examined. It may be prepared by calcining a mixture of boracic acid and nitre. The heat drives off the nitric acid, and leaves a white saline mass, which, when dissolved in water, yields crystals of borate of potash in rectangular four-sided prisms, terminated by dihedral summits. It is capable of combining with an excess of base, and forming a diborate of potash.
- 25. Silicate of potash. Silica and potash certainly unite together in various proportions. But these combinations have

Annals of Philosophy, xv. 86. + Ann. de Chim. et de Phys. xix. 365.

Sect. 11.

not been sufficiently studied to admit of description. When one part of silica and four parts of hydrate of potash are fused together, and cooled very slowly, pouring off a portion of liquid matter, after it has begun to solidify round the edges we obtain silicate of potash in pearly crystals, which are composed of

This silicate is soluble in water, and constitutes the *liquor* silicum of the ancients.

Glass is nothing else than a combination of silica with potash or soda. When there is nothing present but silicate of potash or soda the glass is soluble in water. The mixture of silicates of lime, magnesia, or alumina, or any earthy silicate destroys this solubility.

Fuchs has lately introduced the use of what he calls soluble glass as an excellent substance for rendering wood, cloth, paper, &c., difficult to be burnt. It is formed by fusing together in a clay crucible 10 parts of carbonate of potash, 15 of quartz, reduced to fine powder, and 1 part of charcoal, and keeping up the heat about six hours. The use of the charcoal is to destroy the carbonic acid of the carbonate, which would not be expelled without a very violent heat. The matter thus formed attracts the moisture of the air, and acquires a dull aspect. is completely dissolved when boiled three or four hours with five times its weight of water. The solution may be concentrated to a thick syrup when its specific gravity is 1.25. When this syrup mixed with finely levigated chalk, bone ashes, clay, glass, &c., is laid upon wood, or cloth, or paper, and allowed to dry, it renders them incombustible or nearly so. White lead mixed with it cannot be applied to wood, because it scales off on drying, but it is an excellent application for cloth or paper.

26. Seleniate of potash. This salt is obtained when one part of selenium is intimately mixed and detonated with two parts of nitre, the residue dissolved in water and crystallized. Mitcherlich, to whom we are indebted for the knowledge of this salt, informs us that it exactly resembles sulphate of potash, and that it contains no water of crystallization. Its constituents are

1 atom selenic acid . . . 8
1 atom potash . . . . . . 6

- 27. Selenite of potash. This salt is exceedingly soluble in water. When concentrated sufficiently, the surface becomes covered with a crystalline pellicle. When evaporated to dryness, the salt attracts moisture from the atmosphere. At a red heat it melts and becomes yellow; but recovers its white colour on cooling. It is insoluble in alcohol.
- 28. Biselenite of potash crystallizes (with difficulty) when sufficiently concentrated. The crystals are feather-shaped. It deliquesces when exposed to the air and dissolves in a small proportion in alcohol. When long exposed to heat, one half of the acid is driven off and it is reduced to neutral selenite.
- 29. Quaterselenite of potash does not crystallize, and when
- evaporated to dryness speedily deliquesces again.\*

  30. Antimoniate of potash. This salt may be obtained by exposing a mixture of 1 part of powdered antimony and 6 parts of nitre to the greatest heat which it can bear without fusion. It is then to be reduced to powder and washed with cold water till all the alkali and nitre are dissolved. The residue being now boiled in water, the antimoniate of potash dissolves, while a mixture of oxide of antimony and binantimoniate remains undissolved. The aqueous solution is colourless. It has a weak metalline taste; but is scarcely alkaline if the mass was well washed with cold water. Acids throw down from it a binantimoniate of potash. When evaporated to dryness it leaves a honey yellow transparent substance, which becomes white when all the water is driven off. It is scarcely soluble in cold water, but is completely dissolved in boiling water.
- 31. Antimonite of potash. Berzelius formed this salt by fusing together white oxide of antimony and caustic potash. He then washed off the potash by means of cold water, and dissolved the powder that remained in boiling water. This water when evaporated yields the salt in a state of purity. Its properties are very similar to those of antimoniate of potash.
- 32. Tellurate of potash. If oxide of tellurium be mixed with nitre, and the mixture be exposed to heat, the nitre at first melts without acting on the oxide. But at the temperature in which the oxide begins to liquefy, it decomposes the saltpetre with a violent effervescence, the nitric acid is driven off, and the oxide dissolves in the potash. The mass when cold very much resembles an enamel. It dissolves in boiling water and the solution on cooling deposites an imperfectly crystallized white powder. This is tellurate of potash. It dissolves in

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 257.

M'

small quantity in cold water, and in much greater proportion in boiling water.\* The hot solution deposites the salt in powder on cooling. It has a slight metallic taste, and acts feebly as an alkali on vegetable blues.† When a few drops of nitric acid are let fall into the aqueous solution, a bitellurate of potash precipitates in a white powder, which reddens vegetable blues.

33. Chromate of potash. This salt obtained by saturating chromic acid with potash has a very fine yellow colour. It crystallizes in oblique four-sided prisms, terminated by four-sided pyramids. Two of the opposite lateral edges of the prism

are often replaced by tangent planes. The figure in the margin exhibits one of its most common forms. M and M' represent the primary faces of the prism, they meet, according to the measurement of Mr. Brooke, at angles of 107° 26′. Mr. Brooke‡ considers the primary form to be a right rhombic prism, the above being the large angle of the prism. The following are Mr. Brooke's measure-

ment of some of the other angles of the crystal: .

M on b		•	133°	52'
M on h	•	•	126	17
h on $c$	•	•	119	43
c on c'	•	•	120	34

The crystals are not altered by exposure to the air. Their colouring power is so great that one grain dissolved in 40,000 grains of water forms a solution, having a perceptible yellow colour. If we dissolve one grain of this salt and 20 grains of saltpetre in water, and evaporate the solution, we obtain crystals of saltpetre, almost as deep coloured as chromate of potash itself.

The taste of the salt is cooling and bitter, and very disagreeable, and the impression continues very long in the mouth. 100 parts of water at 60° dissolve 48.368 parts of this salt. Boiling water dissolves any quantity whatever. It is insoluble in alcohol. Its specific gravity is 2.6115. It may be heated to 400° without any change. When heated to redness it assumes a crimson colour, but recovers its yellow colour on cooling. When fused, which requires an intense red heat, it becomes permanently green. Hence it seems to be deprived

<sup>\*</sup> According to Magnus, it is quite insoluble in water whether cold or hot.

<sup>+</sup> Berzelius, Nicholson's Journal, xxxvi. 130.

<sup>‡</sup> Annals of Philosophy (2d series), vi. 120.

of a portion of its oxygen. In a red heat it loses about 3 per cent. of its weight owing to the presence of water mechanically lodged between the plates of the crystals. The constituents

of this salt are

1 atom chromic acid l atom potash

12.5\*

34. Bichromate of potash. This salt is obtained when nitric acid is poured into an aqueous solution of the preceding. The colour becomes red, and the bichromate is deposited in beautiful crystals. It is now manufactured in large quantities in Glasgow and other places for the use of the calico printers.

The crystals are rectangular or square prisms, sometimes terminated by four-sided pyramids. The colour is an intense orange red of the greatest splendour. It is not altered by exposure to the air. The taste is cooling, bitter, and metallic, and it leaves a hot impression in the mouth which does not last nearly so long as that of the chromate. At the temperature of 63° 100 parts of water dissolve 10.44 grains of it. It is insoluble in alcohol. The aqueous solution reddens vegetable blues.

The specific gravity of this salt is 1.9801. When 100 parts of the salt were kept for an hour in the temperature of 400°, the loss of weight was six grains, proceeding from water mechanically lodged between the plates of the crystals. At a red heat it melted into a transparent red liquid without any farther loss of weight. It is still perfectly soluble in water. constituents of bichromate of potash are

2 atoms chromic acid	•	•	13
l atom potash .	•	•	6
			***************************************
			19+

When a solution of lead in nitric acid is fixed upon cotton cloth, and the pieces afterwards passed through an aqueous solution of bichromate of potash, it is immediately dyed of a beautiful and fixed yellow colour. By the same salt several very beautiful purple colours are also obtained, all of them quite fixed. On many of the workmen whose hands are exposed to the solution of this salt, painful sores are produced which are very difficult to heal. Upon others it produces no such deleterious effect.

<sup>\*</sup> Annals of Philosophy, xvi. 321. † Ibid. 325.

- 35. Molybdate of potash. This salt crystallizes in small right rhombic prisms. The taste is metallic and astringent, and somewhat alkaline, and I was unable to obtain it in a state which did not render cudbear paper violet. In my laboratory the crystals slowly deliquesced. But Berzelius, who probably experimented in a dryer place, found them unalterable in the air. The salt is very soluble in boiling water, and the solution is transparent and colourless. The liquid on cooling deposites a salt which seems to be a bimolybdate of potash. A similar salt is deposited in a white powder when a current of chlorine is passed through an aqueous solution of molybdate of potash. It is insoluble in cold, but pretty soluble in boiling water.
- 36. Tungstate of potash. This salt may be formed by dissolving oxide of tungsten in the solution of potash or carbonate of potash. The solution always retains an excess of potash, refusing to dissolve the oxide before the alkali be completely neutralized. By evaporation the tungstate of potash precipitates in the state of a white powder.

This salt has a metallic and caustic taste; it is soluble in water, and very soon deliquesces when exposed to the air. Its solution in water is decomposed by all the acids: they occasion a precipitate of bitungstate of potash, which is the tungstic acid of Scheele.\*

- 37. Titaniate of potash. This salt may be obtained by mixing carbonate of potash finely powdered with titanic acid, fusing the mixture in a platinum crucible, and keeping it in fusion till all gaseous matter ceases to be evolved. If an excess of alkali has been employed, we find in the crucible two layers; the uppermost of carbonate of potash, and the undermost titaniate of potash. Water decomposes this titaniate by carrying off the greatest part of the alkali.+
- 38. Columbate of potash. This salt may be obtained by fusing together a mixture of columbic acid and carbonate of potash as in the formation of the preceding salt. The fused mass is to be well washed with cold water and then dissolved in boiling water. When the solution is evaporated we obtain a saline mass, which does not crystallize, and which may be dissolved in water. It has a weak, but disagreeable metallic taste. The solution is precipitated by all the acids, even by the carbonic.
- 39. Uraniate of potash. This salt is obtained when any salt of peroxide of uranium is precipitated by an excess of caustic

<sup>\*</sup> Vauquelin and Hecht, Jour. de Min. No. 19. p. 20. † H. Rose.

potash. The salt precipitates in a yellow powder, which, when heated to redness, loses its water of crystallization and becomes yellowish red.

The only combination of peroxide of uranium and potash which I was able to obtain by digesting caustic potash or carbonated peroxide of uranium, was a biuraniate, composed of

2 atoms peroxide	e of w	raniur	n.	•	56
1 atom potash	•	•		•	6
3 atoms water	•	•	•	•	3.375
		<i>.,</i>	r		65:375*

40. Manganate of potash. This salt may be obtained by mixing equal weights of binoxide of manganese and hydrate of potash, and exposing the mixture to a red heat for some time in an open platinum crucible. When cold, a very small quantity of water is poured upon the mass. The red solution is decanted off and immediately concentrated till small crystalline needles begin to appear. It is then set aside in a warm place and large crystals of manganate of potash are deposited. The crystals are needle-form, and about half an inch in length. They have a deep purple colour, and may be kept in a dry state. The taste is sweet and slightly astringent. When dissolved in water the colour of the solution is a beautiful purple.

When a large excess of potash is employed in making the salt, or when potash is added to the aqueous solution, the colour becomes green. M. Forchhammer ascribed the green colour to a lower degree of oxidizement of the acid; and this view of the subject has been confirmed by the latter experiments of Mitcherlich. But farther elucidation is necessary to enable us to form a definite opinion on the subject. I have stated in the first volume of this work, while treating of manganese, the present state of our knowledge of these compounds. The manganate of potash was first obtained in crystals by Chevillot and Edwards.

41. Oxalate of potash. This salt is easily formed by saturating oxalic acid with carbonate of potash, and concentrating the solution to the requisite degree. The salt crystallizes in right rhombic prisms with angles of 60° and 120°. The taste of the salt is cooling and slightly bitter. Its specific gravity 2.034. When heated, it loses water and falls to powder. At the temperature of 50° 100 parts of water dissolve 45 parts of

<sup>\*</sup> First Principles, ii. 29.

this salt. When well dried, and exposed in a damp place, it absorbs a little moisture from the atmosphere. A red heat decomposes the acid and leaves carbonate of potash, while carbonic oxide gas makes its escape. Its constituents are

1 atom oxalic acid . . 4.51 atom potash . . . 6
1 atom water . . 1.125

11.625

42. Binoxalate of potash. This salt exists ready formed in oxalis acetosella, or wood sorrel, and in the rumex acetosa; from which it is extracted in some parts of Europe in great quantities. Hence it is known by the name of salt of wood-sorrel, and in this country is sold under the name of essential salt of lemons. It is mentioned by Duclos in the Memoirs of the French Academy for 1668. Margraff first proved that it contained potash; and Scheele discovered its acid to be the oxalic. A great many interesting experiments had been previously made on it by Wenzel and Wiegleb. It is usually prepared by reducing the expressed juice of the oxalis acetosella, or rumex acetosa, to the consistence of a syrup, and setting it aside to crystallize. The brown crystals are purified by a second crystallization. It is manufactured in the large way in Switzerland and some parts of Germany.

The crystals are rhomboids slightly oblique and approaching to cubes. The specific gravity of these crystals is 2.444. The taste is excessively acid. It is chiefly employed to take ink stains out of linen. It is soluble in about ten times its weight of boiling water, but much less soluble in cold water. It is not altered by exposure to the air. Heat decomposes it. The salt is capable of combining with most of the alkalies and earths, and of forming with them double salts, which have not been accurately examined. Dr. Wollaston first showed that it contains exactly double the proportion of acid which oxalate of potash contains. Vogel of Bareuth proved that it contains 12.63 per cent. of water. Its-constituents are

2 atoms oxalic acid	•	•	9
l atom potash	•	•	6
2 atoms water	•	•	2.25

17.25

43. Quateroxalate of potash. This salt was discovered by Dr. Wollaston. When nitric or muriatic acids are made to

Chass I. act upon binoxalate of potash, they deprive it of one half of its alkali. There remains behind an oxalate containing exactly four times the proportion of acid that exists in oxalate of potash. Hence the name given it by Dr. Wollaston. This salt may be purified by a second crystallization. Its crystals are octahedrons having both their apexes truncated pretty deeply. three parts of it be decomposed by a red heat, and the alkali thus evolved be added to I part of the quateroxalate, it will just convert it into a neutral oxalate.\* Its specific gravity is 1.377. Its taste is very sour, and it is less soluble in water than binoxalate. Its constituents, by my analysis, are

> 4 atoms oxalic acid . 1 atom potash 6 7 atoms water 7.875

31.875

44. Acetate of potash. Pliny is supposed, but probably without any reason, to have been acquainted with this salt, because he recommends a mixture of vinegar and vine ashes as a cure for a particular species of tumour.+ It was first clearly described by Raymond Lully. It has received a great number of names; as, for instance, arcanum tartari, secret foliated earth of tartar, essential salt of wine, regenerated tartar, diuretic salt, digestive salt of Sylvius. It is usually formed by dissolving carbonate of potash in distilled vinegar, and evaporating the solution to dryness in a moderate heat. The solution when concentrated ought to be filtered through animal charcoal, provided distilled vinegar has been employed in its preparation. By this process it is obtained in fine white plates. By a well managed evaporation it may be procured in regular prismatic crystals. This salt has a sharp warm taste. At the temperature of 60°, 100 parts of it are soluble in 102 parts of water.§ It is soluble also in alcohol. When exposed to the air, it deliquesces rapidly. When heated, it readily melts, and in a high temperature its acid is decomposed. Its constituents, as determined by Synthesis, are

1 atom acetic acid	•	•	6.25
1 atom potash	•	•	6
2 atoms water	•	•	$2 \cdot 25$
			14.5

<sup>\*</sup> Wollaston on superacid and subacid salts. Phil. Trans. 1808.

<sup>†</sup> Plinii, lib. xxiii. proœmium. † Figuier, Ann. de Chim. lxxxvi. 44.

<sup>§</sup> Speilmann. || First Principles, ii. 258.

45. Binacetate of potash. This salt is easily obtained by dissolving 8.75 parts of dry carbonate of potash in 12.75 parts of crystallized acetic acid previously dissolved in water. The solution crystallizes with facility in large transparent plates. The taste is acid, and the salt deliquesces rapidly. I found this salt composed of

2 atoms acetic acid 1 atom potash. 6.75 6 atoms water 25.25

46. Formate of potash. This salt resembles acetate of potash, but is not so deliquescent. When heated the water may be driven off and a melted mass remains, containing no water of crystallization. The taste of this salt is saline and bitter. When heated, a portion of the acid is driven off and decomposed. The rest is destroyed, and carbonate of potash remains. Its constituents, in the anhydrous state, are

1 atom formic acid . 4.625 l atom potash

10.625

- 47. Mellate of potash. This salt when neutral forms a fibrous saline mass, in which no crystalline form can be distinguished.\*
- 48. Bimellate of potash. This salt is formed when into a rather concentrated aqueous solution of the neutral salt we drop nitric acid till a white precipitate like cream of tartar appears. This precipitate is bimellate. If the solution be heated, the precipitate is again dissolved, and on cooling, the bimellate deposited in crystals. The usual shape is an irregular six-sided prism, terminated by a bihedral summit. The taste is sour, and it seems not more soluble in water than cream of tartar. When heated, it loses first water of crystallization, and then is suddenly converted into a black charry matter.+ This salt was first noticed by Vauquelin.
- 49. Tartrate of potash. This salt is usually prepared by adding at intervals tartar in powder to a hot solution of carbonate of potash till all effervescence ceases. The solution is then boiled for some time, and afterwards evaporated till a pellicle forms on its surface. The shape of the crystals is a right oblique prism deviating very slightly from rectangular.

<sup>\*</sup> Wöhler, Poggendorf's Annalen, vii. 332. + Ibid.

The inclination of the faces of the prism being very nearly 89° 30′. The obtuse edges of the prism are usually replaced by tangent planes. This salt has an unpleasant bitter taste. Its specific gravity is 1.5567.\* According to Wenzel, it is soluble in its own weight of water at the temperature of 50°, and still more soluble in hot water.† When heated it melts, swells up, blackens, and is decomposed. It contains just half the proportion of acid which exists in tartar. The composition of the large oblique crystals of this salt is

 1 atom tartaric acid
 .
 8.25

 1 atom potash
 .
 6

 2 ātoms water
 .
 2.25

 16.5
 .

But I have obtained the salt in transparent needles destitute of water of crystallization. It may be a question, therefore, whether the water in the large crystals was not mechanically lodged between the plates of the salt.

50. Bitartrate of potash. This salt is obtained, in a state of impurity, incrusted on the bottom and sides of casks in which wine has been kept. It is afterwards purified by dissolving it in boiling water, and filtering it while hot. On cooling, it deposites the pure salt in very irregular crystals. this state it is sold under the name of cream of tartar. This salt attracted the peculiar attention of chemists, probably in consequence of the extravagant encomiums and invectives bestowed on it by Paracelsus. It is called tartar, says he, because it produces the oil, water, tincture, and salt, which burn the patient as hell does. According to him, it is the principle of every disease and every remedy, and all things contain the germ of it. This ridiculous theory was combated by Van Helmont, who gives a pretty accurate account of the formation of tartar in wine casks. It was known to Van Helmont, and even to his predecessors, that potash could be obtained from tartar; but it was long a disputed point among chemists, whether that alkali existed in it ready formed. hamel, Margraff, and Rouelle, at last established that point beyond a doubt; but the other component part of tartar was unknown, or very imperfectly known, till Scheele pointed out the method of extracting it.

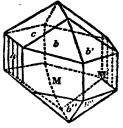
<sup>\*</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

<sup>†</sup> Verwandtschaft, p. 308.

<sup>‡</sup> Tartari Vini Historia, Van Helmont, p. 224.

The crystals of tartar are very small and irregular. But by \_sect. 11.

careful evaporation it may be obtained in irregular six-sided prisms. Mr. Brooke considers the primary form to be a right rhombic prism, the faces of which meet at angles of 107° 30′. The figure in the margin represents the most common crystalline shape. The following are the measurements of the angles according to Mr. Brooke.\*



M on M'	,	•	107° 30		
M on h	•	• .	126	15	
'M on b		•	117	2.	
c on h	•	•	125	<b>30</b>	
c on c		•	109	0	
b on <i>b</i> "	•	•	77	0	

Tartar has an acid and rather unpleasant taste. It is very brittle, and easily reduced to powder. Its specific gravity is 2.4. At 60°, 1 part of tartar dissolves in 234.6 of water. When boiled in water, the liquid takes up nearly 11 th part of the salt. It is not altered by exposure to the air; but when its solution in water is allowed to remain for some time, the salt is gradually decomposed, a mucous-matter is deposited, and there remains in solution carbonate of potash coloured with a little oil. This decomposition was first accurately described by Berthollet in 1782.‡

When tartar is heated, it melts, swells, blackens, and the acid is entirely decomposed. The same changes take place when the salt is distilled in close vessels. The phenomena of this distillation have been described with great care, and its products very attentively examined by chemists; because, before the discovery of the tartaric acid by Scheele, distillation was the only method thought of for obtaining any knowledge of the acid part of tartar. These products are an enormous quantity of gas, consisting of carbonic acid and carburetted hydrogen, an oil, and an acid; and, according to some chemists, carbonate of ammonia. The acid obtained is called pyrotartaric acid.

The tartar of commerce is never quite pure. All the specimens which I had an opportunity of examining contained rather more than 5 per cent. of tartrate of lime. A number of

11.

<sup>\*</sup> Annals of Philosophy (2d series), vii. 161.

<sup>†</sup> Wenzel, Verwandtschaft, p. 311. † Mem. Par.

specimens were examined by Vauquelin and Boullay; they found the tartrate of lime to vary from 5 to 6 per cent.\* Its constituents are

2 atoms tartaric a	acid	•	16.5
1 atom potash	•	•	6
2 atoms water	•	•	2.25
			94.75

51. Vinate of potash. This salt has a weak saline taste, and is very soluble in water.+

52. Bivinate of potash. This salt crystallizes in striated prisms or grains. It has an acid taste, and is dissolved with difficulty in water.

53. Pyrotartrate of potash. It crystallizes in plates, deliquesces in the air, and dissolves in alcohol.

There seems from the experiments of Fourcroy and Vauquelin to be no bipyrotartrate of potash.

- 54. Citrate of potash. This salt may be formed by dissolving carbonate of potash in citric acid, and evaporating the solution to the requisite consistency. It is very soluble in water; does not crystallize easily; and readily deliquesces when exposed to the air.
- 55. Pyrocitrate of potash crystallizes in small white needles, not altered by exposure to the air, and soluble in about four times its weight of water. The solution does not precipitate nitrate of barytes or nitrate of silver, while citrate of potash throws down both of these salts.§
- 56. Malate of potash. Does not crystallize, deliquesces, and is soluble in alcohol.
- 57. Bimalate of potash. This salt crystallizes. The crystals are not altered by exposure to the air, and are insoluble in alcohol.
- 58. Pyromalate of potash. Forms fern-shaped crystals which deliquesce in the atmosphere.\*\*
- 59. Fungate of potash. Does not crystallize, dissolves readily in water, but is not soluble in alcohol. ††
- 60. Mucate of potash. It forms small crystalline grains, very little soluble in water.‡‡ They are not altered by exposure to the air, and do not dissolve in alcohol.§§
  - 61. Pyromucate of potash. It crystallizes with difficulty.

<sup>\*</sup> Ann. de Chim. lxii. 41. + Walchner. 

‡ John and Walchner.

<sup>§</sup> Lassaigne, Ann. de Chim. et de Phys. xxi. 104. | Braconnot.

<sup>¶</sup> Donovan. \*\* Lassaigne. †† Braconnot. ‡‡ Scheele. §§ Trommsdorf.

When concentrated it concretes on cooling into a granular mass, which attracts moisture from the air, and which is very soluble in water and alcohol.\*

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- 62. Succinate of potash. It crystallizes in small prisms, which absorb moisture from the atmosphere, and decrepitate when heated.
- 63. Benzoate of potash. It crystallizes in feather-shaped crystals. It has a sharp saline taste, is very soluble in water, and deliquesces when exposed to the air.
- 64. Bibenzoate of potash. It crystallizes in small plates and needles, which require ten times their weight of cold water to dissolve them. It reddens vegetable blues, and has an acid and sweetish taste. When heated to redness part of the acid sublimes without decomposition, but part likewise is destroyed. An empyreumatic oil is formed, and some charcoal remains mixed with carbonate of potash.†
- 65. Croconate of potash. This salt crystallizes in small needles. It has a lemon-yellow colour, and is easily reduced to a rather deep yellow powder. Taste similar to that of saltpetre. It has no smell, and does not affect vegetable blues. When heated the salt loses its water of crystallization considerably under the temperature of 212°. Its constituents, according to the analysis of Leopold Gmelin, to whom we are indebted for the discovery of this salt, are

1 atom croconic a	atom croconic acid			7.75
1 atom potash		•	•	6
2 atoms water	•	•	•	2.25
				10

- 66. Gallate of potash. This salt is said to be colourless. But when I saturated carbonate of potash with gallic acid the solution became black and opaque. When evaporated I got a black matter, which amounted very nearly to the original weight
- black matter, which amounted very nearly to the original weight of the potash and gallic acid employed.

  67. Meconate of potash. Oblique four-sided prisms, soluble
- 67. Meconate of potash. Oblique four-sided prisms, soluble in twice their weight of water. .
- 68. Boletate of potash. Not easily crystallized. Easily soluble in water, difficultly in alcohol.‡
- 69. Camphorate of potash. This salt crystallizes in small sixsided prisms. Its taste is slightly saltish, bitterish, and aromatic. When exposed to the air it becomes opaque. When

<sup>\*</sup> Houton Labillardicre. † Bucholz, Ann. de Chim. lxxxiv. 311.

<sup>†</sup> Braconnot.

heated it fuses in its water of crystallization and becomes brownish. It dissolves in 100 times its weight of cold and in 4 times its weight of boiling water. It is soluble in alcohol, and the solution burns with a deep blue flame. When exposed to a moist air, it loses a little of its transparency; but in dry air it suffers no change. When exposed to heat it melts, swells, and the acid is volatilized in a thick smoke, which has an aromatic odour. Before the blow-pipe it burns with a blue flame, and the potash remains behind in a state of purity.\*

- 70. Suberate of potash. This salt ought to be formed by means of crystallized carbonate of potash. It crystallizes in prisms, having four unequal sides. It has a bitter saltish taste, and is quite neutral. It is very soluble in water. Heat melts it, and at last volatilizes the acid.† Brandes found it very difficult to obtain it in regular crystals.
- 71. Stearate of potash. To form this salt we must heat in a glass capsule 2 parts of stearic acid with 2 parts of potash prepared by alcohol. When the combination has taken place the vessel is removed from the fire. On cooling the stearate of potash separates from the liquid which retains only the excess of potash. Wrap it up in blotting paper, and subject it to Then dissolve it by heat in 15 or 20 times its weight pressure. of alcohol of the specific gravity 0.821. When the solution cools the salt is deposited in crystals. Let it be thrown on a filter containing no lime, and washed with cold alcohol. in scales which have a great deal of brilliancy, and are quite destitute of colour. 100 parts of boiling alcohol of the specific gravity 0.794 dissolve 15 parts of this salt. One part of it is soluble in 10 of alcohol of the specific gravity 0.821. The solution becomes muddy at 131°, and at 100° the whole becomes At 50° 100 parts of the same alcohol dissolve only 0.432 Ether dissolves it in small quantity, but at the of the salt. same time decomposes it at least partially.

At the usual temperature of the air I part of the salt forms an opaque mucilage with ten parts of water. At 210° this mucilage is completely dissolved. One part of stearate dissolves in 25 parts of boiling water. The solution continues at the temperature of 197° and the liquid may be filtered. On cooling it assumes the form of a viscid jelly. This salt does not absorb oxygen gas.‡

72. Bistearate of potash. To obtain this salt dissolve one

<sup>\* \*</sup> Bouillon Lagrange, Ann. de Chim. xxvii. 24.

<sup>†</sup> Ann. de Chim. xxiii. 52. ‡ Chevreul sur les corps gras, p. 32.

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part of stearate of potash in a sufficient quantity of boiling water, and pour the solution into 1000 parts of cold water. A precipitate of bistearate of potash falls down. Collect it on a filter, let it dry in the open air, and then dissolve it in alcohol. When the solution cools the bistearate is obtained in crystals.

This salt has the form of small needles with a silvery lustre; it has no smell and is soft to the touch. It is scarcely soluble in cold water. When 1 part is boiled in 1000 parts of water an opaque viscid liquid is obtained, which lets fall a quantity of matter as the liquid cools. In this case a portion of stearate is dissolved, and a portion held simply in suspension. Boiling water decomposes this salt, depriving it of a portion of its base. The bistearate is slightly soluble in ether, and the solution is precipitated by the addition of water. Ether deprives it of half its acid and converts it into stearate.\*

- 73. Margarate of potash. To form this salt 1 part of margaric acid and 1 part of hydrate of potash dissolved in five parts of water are heated together. On leaving the mixture at rest the margarate of potash separates from the water, holding the excess of alkali in solution in a semitransparent jelly. Let it be pressed between the folds of blotting paper, then dissolved in 5 parts of boiling alcohol of the specific gravity 0.837, filtered, evaporated to dryness, and the saline residue dried in the temperature of 212°. Thus prepared it is softer than stearate of potash. One part of it exposed for seven days to air, loaded with vapour, imbibes 0.55 of water, and becomes covered with drops. One part at 53° converts 10 parts of water into a translucent jelly. When this jelly is heated to 158° the margarate is quite dissolved. It begins to make its appearance again at 140°, but even at 60° it does not assume immediately the appearance of a stiff jelly. It is insoluble in cold, but dissolves in hot alcohol. It is insoluble in ether.+
- 74. Bimargarate of potash. This salt is obtained by treating margarate of potash in the same way as was described when treating of the formation of bistearate of potash. The salt is obtained in small needles, which are destitute of the silvery lustre that characterizes bistearate. Cold water deprives it of a little alkali. 100 parts of alcohol of the specific gravity 0.834 dissolves 31.37 of this salt at 152°; but at 68° the same quantity of alcohol dissolves only 0.31 of the salt.‡
  - 75. Ricinate of potash. This salt resembles common soap

<sup>\*</sup> Chevreul sur les corps gras, p. 39. † Ibid. p. 63. ‡ Ibid. p. 64.

in its appearance. It is soluble in water and alcohol. The calcareous salts decompose it, as does also common salt.\*

76. Oleate of potash. This salt is prepared by a process similar to that already stated when describing stearate and margarate of potash. One part of oleic acid is heated with one part of hydrate of potash dissolved in five parts of water. The oleate when formed is separated from the water, pressed between folds of blotting paper, and then dissolved in between 10 and 15 times its weight of alcohol, of the specific gravity 0.821. By evaporating the alcoholic solution, we obtain the oleate in a state of purity.

Thus obtained it is a white powder destitute of smell, but having a bitter alkaline taste. One part of it makes a transparent jelly with two parts of water. A great quantity of water partially decomposes it. At 122° alcohol of the specific gravity 0.821 dissolves its own weight of it. The solution becomes muddy at 105°, and at 53° the whole becomes solid. Two parts of the same alcohol dissolve 1 part of the salt and retain it in solution at 53°. When it is set aside for some time crystals of oleate of potash are deposited. 100 parts of boiling ether dissolve 3.43 parts of this salt. The solution remains permanent at 53°. This salt is insoluble in potash ley, and in a concentrated solution of chloride of potassium. It is decomposed by the earthy and metalline salts in general.

- 77. Binoleate of potash. When 103.5 parts of hydrated oleic acid, 9.21 parts of real potash, and 400 parts of water are digested together in a moderate heat, we obtain a gelatinous mass which may be mixed with 1000 parts of water, without solution or separation of oleic acid. In this state the salt is a binoleate of potash. It is soluble in alcohol, and the solution strongly reddens vegetable blues.‡
- 78. Phocenate of potash. This salt is obtained by putting phocenic acid in excess with a solution of potash or carbonate of potash. On evaporation the excess of acid separates. The salt has a sharp and somewhat alkaline taste, leaving a sweet impression like that of phocenic acid. It is exceedingly deliquescent. At the temperature of 68° 100 parts of alcohol of the specific gravity 0.792 dissolve 25.8 parts of this salt, and probably a greater quantity.
- 79. Butyrate of potash. This salt is obtained by neutralizing potash or its carbonate with butyric acid dissolved in water.

<sup>\*</sup> Bussy and Lecanu, Jour. de Pharm. xiii. 68.

<sup>†</sup> Chevreul, sur les corps gras, p. 84. ‡ Ibid. p. 87. § Ibid. p. 110.

It crystallizes confusedly in mushroom or cauliflower like masses at a temperature of between 77° and 86°. Its taste is sweetish, and its smell similar to that of butter. It is very deliquescent, and very soluble in water. At 60° 100 water dissolve 125 of this salt.\*

- 80. Caproate of potash. Obtained by neutralizing carbonate of potash with caproic acid, and leaving the solution to spontaneous evaporation. It is a transparent jelly, which, when heated, assumes the appearance of an enamel.†
  - 81. Hircate of potash is a deliquescent salt.;
- 82. Crotonate of potash crystallizes in rhomboidal prisms and tables, which are not altered by exposure to the air, and which dissolve with difficulty in alcohol of the specific gravity 0.85.§
- 83. Ambreate of potash is a very soluble salt obtained by saturating carbonate of potash with ambreic acid.
- 84. Binambreate of potash. This salt is formed by adding to the solution of the acid in alcohol, an aqueous solution of potash as long as flocks continue to precipitate. When the liquid is farther diluted with water, and set aside, more of the binambreate falls down. This salt is insoluble in water, but it dissolves in alcohol, and reddens litmus paper.
- 85. Cholesterate of potash. A brownish yellow matter which does not crystallize, is very deliquescent, and is insoluble in alcohol and ether. Quite different from soap.¶
- 86. Silvate of potash does not crystallize. It is transparent and dissolves in boiling naphtha, from which it is deposited on cooling in the state of a jelly. When strongly heated it is decomposed, and forms a dark brown fused mass, which is a compound of resin and potash, soluble in water, and acids throw down from the solution a dark brown powder.\*\*
- 87. Bisilvate of potash. This salt resembles bistearate of potash a good deal in its appearance. It may be formed by dissolving silvic acid in six times its weight of absolute alcohol, and boiling the solution for a quarter of an hour over an excess of bicarbonate of potash. Filter the liquid, and set it aside to cool. The bisilvate is deposited in very fine needles. It is soft and woolly like. When heated it melts like a resin, and if the heat be increased it is decomposed, carbonate of potash remaining behind. It is scarcely soluble in water, but it dis-

<sup>\*</sup> Chevreul, sur les corps gras, p. 125. † Ibid. p. 141. ‡ Ibid. p. 151.

<sup>§</sup> Buchner, Repertorium fur die Pharmacie, xix. 185.

Pelletier and Caventou, Jour. de Pharm. vi. 50.

<sup>¶</sup> Ibid. Ann. de Chim. et de Phys. vi. 403.

<sup>\*\*</sup> Unverdorben, Poggendorf's Annalen, xi. 398.

solves in 20 times its weight of cold alcohol, and is still more soluble at a boiling heat. Its solubility in naphtha and olive oil is nearly the same. It is still more soluble in ether and in oil of turpentine. It dissolves readily in a diluted alkaline ley, and is converted into neutral silvate.\*

- 88. Pinate of potash. To obtain this salt boil for a few minutes a solution of pinic acid in ether, over carbonate of potash, filter the solution and evaporate. The salt thus obtained looks like a resin; but it gradually dissolves when boiled in water. Most of the neutral salts throw it down from its solution in water in a white state, and of the consistence of tar. In this state it is a hydrate.
- 89. Carbazotate of potash. This salt crystallizes in long four-sided prisms, translucent, and having a yellow colour and a great deal of brilliancy. At 60° it dissolves in 260 times its weight of water, but is much more soluble in boiling water. A saturated boiling solution solidifies, on cooling, into a mass composed of needles interlaced with each other. When crystallized from a less concentrated solution, the crystals appear by reflected light, sometimes red and sometimes green. The strong acids decompose this salt, yet when carbazotic acid is dropt into a solution of saltpetre, carbazotate of potash is gradually deposited in crystals.

This salt is insoluble in alcohol. When the salt is heated in a glass tube it melts, and soon after is decomposed with an explosion, shattering the glass to pieces. It contains no water of crystallization, but is a compound of

Carbazotic aci	d	•	•	31
Potash		•	•	6
				<b>37</b> ‡

90. Indigotate of potash. This salt is easily obtained by saturating indigotic acid by carbonate of potash, evaporating to dryness, dissolving in hot alcohol, and filtering the solution. The salt crystallizes as the liquid cools. The salt is yellow, very soluble in water, but very sparingly in cold alcohol. It contains no water of crystallization, but is composed of

1 atom indigotic acid	•	•	<b>35</b>
1 atom potash .	•	•	6
			418

<sup>\*</sup> Unverdorben, Poggendorf's Annalen, xi. 398. † Ibid. p. 250.

<sup>‡</sup> Liebig, Ann. de Chim. et de Phys. xxxv. 81. § Buff, ibid. xli. 178.

Rect 1T

- 91. Urate of potash. A white powder nearly similar to uric acid in appearance and solubility. It is soluble in potash ley.
- 92. Pyrurate of potash. A soluble saltwhich may be obtained in crystals.\*
- 93. Aspartate of potash. This salt does not crystallize, it deliquesces when left exposed to the air. It has a sweetish taste with a flavour of beef tea. It is soluble in water. When dropt into the solution of sulphate of copper, it strikes a beautiful sky blue colour, while with perchloride of iron it gives a strong red. It does not precipitate barytes, lime, nickel, or cobalt, or tartar emetic; but it forms a white precipitate when dropt into solutions of acetate of lead, nitrate of mercury, and nitrate of silver.+
- 94. Nitrosaccharate of potash.
  95. Binitrosaccharate of potash.

  Both of these salts crystallize in needles. The taste is cooling, leaving an impression of sweetness. When thrown on red-hot coals they detonate like saltpetre.
- 96. Allentoate of potash crystallizes in beautiful silky needles. It dissolves in about 15 times its weight of cold water. It is decomposed by the mineral acids which precipitate the allentoic acid in the state of a fine powder.§
- 97. Hydrocarbosulphate of potash. This salt crystallizes in long needles, or constitutes a fibrous mass composed of similar crystals. It has a peculiar smell; its taste is a little like that of sulphur, but very strong. It is not altered by exposure to the air, and is very soluble in water and alcohol, but sparingly in other. The solution precipitates most of the metalline salts, but not the salts of barytes and lime. When held to the flame of a candle it catches fire and burns, throwing about a great number of brilliant sparks.
- 98. Sulpho-vinate of potash. This salt crystallizes in glittering scales, somewhat like boracic acid. It has a sweetish taste, is very soluble in water, and melts when gently heated. When heated to redness in a platinum crucible it burns with flame, carbonate of potash being left behind.
  - 99. Sulphonaphthalate of potash. It forms transparent or

<sup>\*</sup> Chevallier and Lassaigne. Ann. de Chim. et de Phys. xiii. 160.

<sup>§</sup> Lassaigne, ibid. xviii. 302.

<sup>|</sup> Zeise, Annals of Philosophy (2d series), iv. 241.

<sup>¶</sup> Dabit, Ann. de Chim. et de Phys. xiii. 66; and Vogel, Gilbert's Annalen, lxiii. 94.

white pearly crystals, which are soft, slightly fragile, are not altered by exposure to the air, and have a bitter and saline taste. They are not very soluble in water, but are not decomposed by frequent solutions and crystallizations. When heated the salt burns with a strong flame. When heated in a glass tube it is decomposed.\*

# SECTION III.—SALTS OF SODA.

In general the salts of soda are much more soluble in water than the salts of potash. Many of the salts of potash contain no water of crystallization, but most of the salts of soda contain a great deal.

When exposed to a red heat they usually speedily melt into a liquid, in consequence of the great quantity of water which they contain. If the heat be continued the water is driven off, and the salt converted into a white powder. When the heat is urged farther, if the acid be of a combustible nature, it is destroyed; if it be volatile, it is driven off; but if it be fixed, the salt melts again at a red heat, and continues in a liquid state as long as the temperature is kept up. The salt, on cooling, is in the state of an opaque white mass, and is usually destitute of water.

No precipitate is produced in solution of salts of soda by tartaric acid, or nitromuriate of platinum; nor does sulphate of alumina added occasion the formation of octahedral crystals of alum: nor is any precipitate produced by infusion of nutgalls or prussiate of potash, except when the basis of the acid happens to be a metal.

One of the easiest methods of ascertaining whether the base of a given salt be soda, is to determine the shape of the crystals which it forms. If it does not shoot into regular crystals, separate the acid by means of sulphuric or nitric acid, and let the new formed salt crystallize. Sulphate or nitrate of soda are easily recognised by the figure of their crystals.

1. Common sulphate of soda. This salt was first discovered by Glauber, a German chemist, and for that reason was long known by the name of Glauber's salt. He himself called it sal mirabile. It may be prepared by saturating soda with sulphuric acid; but it is more usually obtained by decomposing common salt in order to procure muriatic acid. It crystallizes with great readiness. The primary crystal is an oblique rhombic prism. The base of the prism is inclined to the lateral faces at an angle

<sup>\*</sup> Foraday, Annals of Philosophy (2d series), xii. 207.

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of 101° 20′, and the two contiguous lateral faces are inclined to each other at an angle of 80° 24′. The acute lateral edges of the prisms are usually replaced by tangent planes, making the prism six-sided. Sometimes the obtuse lateral edges are replaced by two faces, making the prism eight-sided. The sides of the prisms are usually channelled, and the crystals are almost always exceedingly irregular. Its specific gravity, according to Wallerius, is 2·246;\* Dr. Watson, by a method not susceptible of much precision (on account of the ready solubility of this salt), found it 1·380.†

Its taste at first has some resemblance to that of common salt, but soon becomes very disagreeably bitter. 100 parts of water at the temperature of 60° dissolve 48.66 grains of crystallized salt. When heated to redness so as to drive off its water of crystallization, and then pounded in a mortar, it dissolves in 3.3 its weight of water at the temperature of 144°.‡ When exposed to the air, it loses great part of its water, and falls into a white powder, but it is not otherwise altered. It loses about 56 per cent, of its weight.

When exposed to heat, it first undergoes the watery fusion,¶ then its water is evaporated, it is reduced to a white powder, and in a red heat it melts. Mr. Kirwan has observed, that part of the acid, as well as the water, is driven off by the application of a strong heat.\*\*

Gay-Lussac has discovered that water of the temperature of 91° dissolves a maximum of anhydrous sulphate of soda. At that temperature, 100 parts of water dissolve 50.65 parts of the salt. The solubility diminishes a little as the temperature increases, and 100 parts of water at the boiling temperature dissolve only 42.65 parts of the salt. The solubility diminishes at a still greater rate, as the temperature sinks, so that 100 parts of water at the freezing point dissolve only 5.02 parts of the anhydrous salt. The following table exhibits the results of Gay-Lussac's experiments on the solubility of this salt both anhydrous and crystallized. The temperatures are marked according to the centigrade scale.††

- \* Wallerius' Chemia Physica, 266.
- † Chemical Essays, v. 66. I found the specific gravity of the salt 1.3497.
- # Wenzel, p. 309.
- § Substances which fall to powder in this manner are said to effloresce.
- ₩ Wenzel, p. 312.
- ¶ When substances, on the application of heat, melt by means of the water they contain, they are said to undergo the watery fusion.
  - \*\* Irish Transactions, v. †† Annals of Philosophy, xv. 10.

## Salts soluble in 100 water.

Temperature.			Anhydrous,			Crystals.
0.00°	•	•	5.02	•	•	12.17
11.67	•	•	10.12	•	•	26.38
13.30	•	•	11.74	•	•	31.33
17.91	•	•	16.73	•	•	48.28
25.05	•	•	$28 \cdot 11$	•	•	99.48
28.76	•	•	3 <b>7</b> ·35	•	•	161.53
30.75	•	•	43.05	•	•	215.77
31.84	•	•	47.37	•	•	270.22
32.73	•	•	50.65	•	•	$322 \cdot 12$
<b>33·88</b>	•	•	50.04	•	•	$312 \cdot 11$
40.15	•	•	<b>48.7</b> 8	•	•	291.44
45.04	•	•	47.81		•	276.91
50.40	•	•	46.82	•	•	$262 \cdot 35$
<b>59·79</b>	•	•	$45 \cdot 42$			
70.61	•	•	44.35			
84.82	•	•	42.96			
103.17	•	•	42.65			

## Its constituents are

1 atom sulphuric a	acid	•	•	5
1 atom soda	•	•	•	4
10 atoms water	•	•	•	11.25
				20.25

In the vacuum of an air pump over sulphuric acid, it loses all its water in a few hours.

2. Anhydrous sulphate of soda. When a saturated solution of sulphate of soda at a boiling temperature is concentrated, crystals of sulphate of soda are gradually formed, in which there is no water of crystallization. These crystals are transparent or translucent. They consist of octahedrons composed of two four-sided pyramids united together by a rhombic base. The angles of the rhomb are about 75° and 105°, and the inclination of a face of one pyramid to the corresponding face of the other pyramid about 140°, measured by a common geniometer. These crystals are firm and solid, and have a glassy appearance. Their specific gravity is 2.645. 100 parts of water, at the temperature of 57°, dissolve 10.58 parts of this salt. When the saturated solution is set aside, crystals of common Glauber's salt are formed. When heated to redness the salt undergoes fusion, and, on cooling, concretes into a foliated

brittle saline mass, exactly as happens to common sulphate of sect. III. soda inlike circumstances. The constituents of this salt are

I got the first specimens of this salt which I ever saw, from Mr. W. Wilson of Hurlet, Mr. Harvey afterwards ascertained that the same salt is formed when a saturated solution of glauber salt is kept in a temperature of about 120° in a stove.\*

3. Octohydrated sulphate of soda. When 51 parts of common crystals of common sulphate of soda are dissolved in 49 parts of water of the temperature 150°, and the solution is put aside in a well corked phial, it is well known that it does not crystallize immediately. But in two or three days prismatic crystals are deposited, which are transparent, and have the form of four-sided prisms with dihedral summits. On taking out the cork the whole salt shoots into a fibrous mass, from which the crystals previously formed are easily distinguished, by their at once assuming an opacity and a snow white colour. These crystals are much harder than those of common sulphate of soda. This salt is a compound of

4. Bisulphate of soda. This salt may be obtained by dissolving sulphate of soda in dilute sulphuric acid, and after concentrating it sufficiently setting it aside. The bisulphate crystallizes in oblique four-sided prisms approaching the shape of glauber salt. The crystals do not deliquesce when exposed to the air. But when left upon blotting paper, the paper became gradually moist. The taste of the salt is very acid. When a crystal is held in the flame of a candle it melts like a piece of ice. It liquefies also at 300°, and may be kept long liquid at that temperature without much loss of weight. It may be exposed to a red heat without losing its excess of acid. Its specific gravity is 1.800. At 60° 100 parts of water dissolve 92.72 parts of this salt; so that it is more than twice as soluble as sulphate of soda. Its constituents are

<sup>\*</sup> Annals of Philosophy (2d series), xii. 401.

<sup>+</sup> Faraday, Poggendorf's Annalen, vi. 83: Annals of Philosophy (2d series) xii. 403.

Class	Ł

2 atoms sulphuric a	acid	•	•	10
l atom soda .	•	•	•	4
4 atoms water	•	•	•	4.5
				18.5*

5. Sesquisulphate of soda. This salt may be obtained when the residue after the decomposition of common salt by sulphuric acid in excess is dissolved in hot water and set aside. The first crop of crystals deposited is usually sesquisulphate of soda.

The crystals are transparent prisms, firmer and harder than those of sulphate of soda. They seem to be right prisms with an oblique base. The lateral edges of the prism are sometimes replaced by tangent planes, making the prism eight-sided, and the prism is sometimes terminated by a four-sided pyramid usually truncated at its apex. The taste of the salt is acid. It does not sensibly absorb moisture; but when left on blotting paper, the paper becomes moist and acid, and continues so; but this property is destroyed by washing the crystals with water. The crystals do not effloresce when exposed to the air. The specific gravity is 2.26. At the temperature of 63°, 100 parts of water dissolve about 25of this salt. When the water saturated with it is set aside, crystals of glauber salt are deposited.

When this salt is heated on the sand bath, it does not melt nor alter its appearance, and loses very little weight. Even a red heat occasions very little loss of weight. The salt is anhydrous, and composed of

11	atom	sulphi	ıric ə	cid	•	•	7.5
ı	atom	sođa	•	•	•	•	4

# 11.5+

6. Sulphite of soda. This salt reacts feebly on vegetable colours as an alkali. It is white and perfectly transparent. Its crystals are four-sided prisms, with two very broad sides and two very narrow ones, terminated by dihedral summits. Its taste is cooling and sulphureous. It is soluble in four times its weight of cold water, and in less than its weight of boiling water. By exposure to the air it effloresces, and is slowly converted into a sulphate. When exposed to heat it undergoes the watery fusion. If any confidence can be put in the analyses of Fourcroy and Vauquelin, its constituents are

<sup>\*</sup> Annals of Philosophy (2d series), x. 439.

<sup>+</sup> Ibid. 436.

1 atom sulphur	ous a	cid	•	•	4	Sect. III.
l atom soda	•	•	•	•	4	
8 atoms water	•	•	•	•	9	

7. Bisulphite of soda. If we pass a current of sulphurous acid gas through a solution of carbonate of soda till the liquid reddens vegetable blues, and then concentrate, the liquid bisulphite of soda crystallizes. This salt forms four-sided rectangular prisms. It has the smell of sulphurous acid, strongly reddens vegetable blues, and has an acid and sulphureous taste. Its constituents, as determined by Mr. Thomas Clark, are

2 atoms sulphurous acid			•	•	8	
1 atom soda	•	•	•	•	4	
9 atoms water	•	•	•	•	10.125	

### 22.125

- 8. Hyposulphite of soda. This salt may be formed precisely in the same way as hyposulphite of potash. It crystallizes on cooling, when evaporated to a syrup, in silky tufts, radiating from a centre, which at length extend through the whole liquid, and render it solid. When exposed to the air it deliquesces, but in vacuo along with sulphuric acid it effloresces. Its taste is intensely bitter and nauseous. When heated, it first undergoes the watery fusion, then dries into a white mass, and at length takes fire, burning with a vivid deflagration, and a bright yellow flame. It is insoluble in alcohol, which precipitates it from water. Chloride of silver dissolves in it almost as readily as sugar in water.\*
- 9. Hyposulphate of soda. This salt may be obtained by decomposing hyposulphate of manganese by sulphuret of sodium, and evaporating the liquid to the point of crystallization. To obtain large crystals the best way is to introduce a few crystals into the liquid and then set it aside. It crystallizes in four-sided prisms nearly rectangular, two of the opposite lateral edges of which are usually replaced by tangent planes. A detailed description of the crystals is given by Dr. Heeren of Hamburgh.† The taste is excessively bitter. When heated, it decrepitates slightly. 11 parts of boiling water dissolve 10 parts of this salt, but it requires 2·1 parts of water to dissolve 1 of it at 60°. It is insoluble in alcohol. Its constituents, as determined by Heeren, are

<sup>\*</sup> Herschell, Edin. Phil. Jour. i. 19. † Poggendorf's Annalen, vii. 77.

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1 atom hyposul	phui	ric acid	•	9
1 atom soda		•	•	4
2 atoms water	•	•		$2 \cdot 25$

### 15.25\*

10. Nitrate of soda. This salt was obtained at first by distilling a mixture of common salt and nitric acid in a retort, dissolving the residue in water, and evaporating. It was called cubic nitre, and is occasionally mentioned by the chemical writers of the early part of the last century; but it was Margraff who first analyzed it, pointed out the method of procuring it in a state of purity, and described its properties with accuracy.+ His experiments were afterwards repeated by Dr. Lewis.‡

It may be prepared by direct solution, or by mixing nitrate of lime and sulphate of soda together, filtering the solution, and evaporating. The crystals are transparent, and have a

rhomboidal form.

The figure in the margin represents the shape of the crystal. The following are the measurements according to Mr. Brooke's determination.

P on P' 106° 30′ Pon P" 73 30

This salt is of the specific gravity 2.0694. It has a cool sharp taste, and is somewhat more bitter than nitre. Its solubility, as determined by Marx, is as follows:

Temp.		Salt.
21°,	, 100 parts of water	dissolve 63·1 parts.
32	-	80
<b>50</b>	1	22.7
61		<b>55</b>
246	•	218.5

So that its solubility is more than three times as great at 32°, as at 50°.

As it attracts moisture when exposed to the air, it does not answer for the manufacture of gunpowder. It is sometimes used in fire works, because it communicates a fine orange colour to combustibles while burning. It contains no water of crystallization; but usually about 3 per cent. of water mechan-

<sup>\*</sup> Poggendorf's Annalen, vii. 77. † Opusc. ii. 331.

<sup>†</sup> Phil. Com. p. 642.

Annals of Philosophy (2d series), v. 452.

<sup>||</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

ically lodged between the plates of the crystals. Its constitu-

An immense deposite of it, extending for many miles, is said to exist in the desert of Atacama in Peru. Attempts were made some years ago to introduce it into commerce, but they did not succeed. It might be used with advantage for the manufacture of nitric acid, and probably also in that of sulphuric acid.

11. Hyponitrite of soda may be obtained by the same process as hyponitrite of potash. It has scarcely been examined.
12. Chlorate of soda. Mr. Chenevix must be considered as

12. Chlorate of soda. Mr. Chenevix must be considered as the first chemist who published a description of this salt; for the short notice of Dolfuz and Gadolin\* scarcely conveys any precise information. It may be prepared by the same process as chlorate of potash; but it is difficult to obtain it pure, as it is nearly as soluble in water as muriate of soda. Mr. Chenevix procured a little of it pure by dissolving the mixtures of muriate and chlorate of soda in alcohol, and crystallizing repeatedly. But the easiest mode of preparing it is to dissolve carbonate of soda in chloric acid. It does not crystallize till it be reduced almost to a syrupy consistence. Its crystals are square plates, similar to those of chlorate of potash.† Its taste is very sharp and cooling. On burning coals it melts into globules, and produces a yellow light. According to Vauquelin, 500 parts of dry carbonate of soda produce 1100 parts of crystallized chlorate of soda.

When distilled it gives out oxygen gas mixed with some chlorine, and the salt which it leaves behind has alkaline properties. It is composed of

1 atom chloric acid . . . 9.5 1 atom soda . . . 4

13.5

- 13. Bromate of soda, as appears from the experiments of Balard, crystallizes in prisms.
  - 14. Iodate of soda. This salt is prepared in the same way
  - \* Ann. de Chim. i. 227.

<sup>†</sup> According to Mitcherlich, they are tetrahedrons or rhombs very little oblique.

Class I,

as iodate of potash. It is deposited in small grains and is anhydrous. It melts when heated like nitre, and gives out oxygen gas and leaves an iodide of sodium. 100 parts of water at about 58° dissolve 7.3 of this salt. Its constituents are

1 atom iodic acid . . . 20.75
1 atom soda . . . 4

24.75

15. Di-iodate of soda. This sait may be obtained by treating the preceding with the requisite proportion of caustic soda. It is more soluble, has an alkaline taste, and contains a great deal of water of crystallization. It is not altered by exposure to the air. When heated it melts, and detonates feebly with burning coals.

16. Carbonate of soda. This salt has been also very long known. It is usually obtained by burning and lixiviating marine plants, or by decomposing common salt. In commerce it is called barilla or soda. In that state, however, it is never perfectly pure, containing always a mixture of earthy bodies, and usually common salt; but it may be purified by dissolving it in a small portion of water, filtrating the solution, and evaporating it at a low heat, skimming off the crystals of common salt as they form on its surface.\*

Of late years prodigious quantities of carbonate of soda have been manufactured from common salt; the price has fallen to less than one third of what it was formerly, and it is gradually taking the place of potash in those manufactures that require an alkali. The process followed in this country is to convert common salt into sulphate of soda by means of sulphuric acid.† The sulphate of soda is heated with sawdust or small dross of pit coal, by which it is converted into sulphuret of sodium. Sometimes the sulphur is got rid of by means of lime, but more commonly by roasting the sulphuret, so that the air from a coal fire passes through it. The sulphur is gradually dissipated, and the sodium converted into carbonate of soda. The matter thus treated is dissolved in water and subjected to two succes-

<sup>\*</sup> See a detail of the different plants from which this substance is procured, and of the method of procuring them, in the Ann. de Chimie, Vol. xlix. 267.

<sup>†</sup> This decomposition takes place in some of the largest manufactures during the formation of bleaching powder, so that the sulphate of soda is at first mixed with sulphate of manganese. This last salt is got rid of by fusing the whole matter in a furnace.

sive crystallizations in open iron coolers. By this process beautiful crystals of carbonate of soda are obtained. They in general contain about half a per cent. of sulphate of soda.

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The crystals of carbonate of soda are very large, being frequently 8 or 9 inches long. They have usually the form represented in the margin. The primary form seems to be an oblique rhombic prism. The apex of this prism is not visible in the common crystal; but it makes angles of 108° 43' with the faces of the prism. M, M' the two primary faces of the prism meet at angles of 76° 12'. The following are the measurements of the angles, according to Mr. Brooke.\* In them P denotes the base of the primary prism.

P on M or	$\mathbf{M'}$		•	108°	43'
P on e or e	e <b>'</b>	•	•	129	52
P on h	•	•	•	121	20
M on M'	•	•	•	76	12
M on h		•	•	128	6
M on k		•	•	141	<b>54</b>
e on e'			•	<b>79</b>	44
e on k	•	•	•	140	8

Its taste is precisely the same with that of the carbonate of potash, but less caustic. Its specific gravity is 1.623 by my trials. The specific gravity of a saturated solution at 58°.25, 1.07516. 100 grains of this solution evaporated to dryness left 7.19 grains, hence at the temperature of 58° 100 parts of water dissolve 7.74 grains of the anhydrous salt, or 20.64 of the crystals. It dissolves in rather less than its weight of boiling water, so that when dissolved in boiling water it crystallizes as the solution cools. When exposed to the air, it very soon effloresces and falls to powder. When heated, it undergoes the watery fusion; indeed the soda of commerce sometimes contains so much water of crystallization, that, when once melted, it remains permanently liquid. If the heat be continued, the water gradually evaporates, and the salt becomes dry. In a red heat it melts into a transparent liquid. A very violent heat drives off a part of its acid. This salt melts rather more easily than carbonate of potash, and for that reason it is preferred by glass manufacturers. Its constituents are

<sup>\*</sup> Annals of Philosophy (2d series), vi. 287.

1 atom carbonic	acid	•		2.75
1 atom soda	•	•		4
10 atoms water			•	11.25
r				
				10

17. Protohydrated carbonate of soda. This salt was obtained by Mr. Harvey. It crystallized in a saturated solution of common carbonate of soda kept for a long time in a temperature of 120°. The crystals are transparent, and consist of thin rectangular prisms terminated at either extremity by a bevelled summit. Specific gravity 2·262. The crystals were harder and firmer than those of common carbonate of soda. Not altered by exposure to the air. These crystals contain no other impurity than a trace of common salt. I found the constituents in three successive analyses.

Carbonic	c acid	•	•	7.5
$\mathbf{Soda}$	•	•	•	9.412
Water	•	•	•	2.93
				19.842
Loss	•	•	•	0.158
	-			20.000

This is equivalent to

3.188 carbonic acid,

4 soda,

1.245 water, including a little muriatic acid. The salt then contains a slight excess of carbonic acid; unless we are to ascribe this excess to an error in the analysis. The constituents are obviously

1 atom	carbon	ic a	cid	•	2.75
1 atom	$\mathbf{soda}$	•	•		4
1 atom	water	•	•	•	1.125
					7.075

18. Sesquihydrated carbonate of soda. This salt is described in Poggendorf's Annalen by Mohs, under the name of prismatic carbonate of soda.\* It is obtained when a saturated solution of carbonate of soda at a temperature of from 68° to 86° is allowed to cool. The crystals are four-sided tables, they effloresce in the air, but much more slowly than common

carbonate. Its composition, according to the analysis of Hai- Sect. 111. dinger is

Anhydrous carbonate of soda . 82.26 Water . . . . . . 17.74

100.00

This amounts to about  $1\frac{1}{4}$  atom water. But I am rather disposed to consider the water as amounting at first to  $1\frac{1}{2}$  atom. This would make the constituents

1 atom anhy	6.75	
11 atom water	1.687	5
	<del></del>	_
	8.437	5

19. Octohydrated carbonate of soda. This salt crystallized in Mr. Tennant's carbonate of soda leys during the very hot summer of 1825. It crystallizes in large right rectangular prisms usually terminated by a four-sided pyramid. Two opposite faces of the prism are much larger than the other two. The same remark applies to the pyramidal termination. The inclination of the small faces of the pyramid to the corresponding face of the prism is about 115°, that of the large faces 150°. 100 parts of water at 63° dissolve 63.87 of these crystals. When heated, the salt partly liquefies, but not completely. It did not effloresce in my laboratory, which was rather damp. Its specific gravity was 1.51. Its constituents were found on analysis to be

1 atom carbonic	e acid	•	•	2.75
1 atom soda			•	4
8 atoms water	•			9

15.75\*

20. Sesquicarbonate of soda. Though this salt occurs native in Africa in considerable quantities, it was not distinguished from the soda of commerce till, in 1802, Klaproth published an account of it in the third volume of his works.† It is found in the province of Sukena near Fezzan, and is called trona by the natives. It is crystallized in hard striated masses, not altered by exposure to the air, and of such hardness that the walls of Cassar, a fort now in ruins, are said to have been built of it. It may be formed artificially by exposing the common carbonate of soda to an atmosphere of carbonic acid gas.

<sup>\*</sup> Annals of Philosophy (2d series), x. 442.

<sup>†</sup> Beitrage, iii. 83.

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It is manufactured in London for the soda water makers, and is usually sold in the state of a white powder; but I have crystallized it in the form of doubly oblique four-sided prisms, with angles of about 60° and 120°. Its taste is alkaline, but much milder than common carbonate. Specific gravity 1.980. Its constituents, as determined by Mr. Phillips, are

1 atom carbonic	acid	•	4.125
1 atom soda .	٠,	•	4
2 atoms water	4	•	$2 \cdot 25$

10.375\*

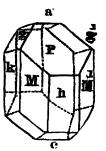
21. Bicarbonate of soda. This salt was made and analyzed many years ago by Rose, and afterwards by Berthollet. I obtained it with ease by suspending a solution of common carbonate of soda over a brewer's fermenting tun during the fermentation of beer. It crystallizes in oblique rectangular prisms. The taste is feebly alkaline. It gives a purple colour to cudbear paper, and restores the blue colour to litmus paper reddened by vinegar; but its alkaline properties are very weak. At the temperature of 64°, 100 parts of water dissolve 9.33 parts of this salt. Its constituents are

2 atoms carbon	nic	acid	•	<b>5</b> ·5
1 atom soda	•	•	•	4
l atom water	•	•	•	1.125

10.625+

22. Phosphate of soda. This salt is usually prepared by saturating phosphoric acid (obtained from burned bones) with carbonate of soda till the liquid reacts as an alkali, and set-

ting the concentrated solution aside to crystallize.



The crystals are oblique rhombic prisms with angles of about 67° 50′. The base of the prism is inclined to the lateral faces at an angle of 106° 44′. One of the most common modifications is represented in the margin. The following are the measurements of the various angles, as determined by Mr. Brooke.‡

uiigics,	us uc	OCI MAIA	LICU D	<i>y</i>
P on M or	· M'	•	•	106° 44′
P on c	•	•	•	129 12
$\mathbf{P}$ on $g$	•	•	•	112 27
P on h	•		•	121 14

<sup>\*</sup> Quarterly Journal, vii. 296. † First Principles, ii. 267.

<sup>‡</sup> Annals of Philosophy (2d series), vi. 286.

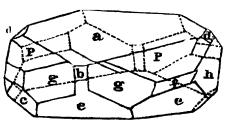
M on M' . . . . 67° 30'
M on h . . . . 123 45
M on k . . . 146 15

Sect. IIL

The taste of this salt is saline and not strong. ces with great rapidity when exposed to the air, becoming white and opaque, but not losing its shape. When heated it melts in its water of crystallization, and after the water has been driven off the anhydrous salt easily melts when heated It is readily soluble in water. 100 parts of water to redness. at 65° dissolve 26.77 parts of the salt. It has no effect on litmus, but renders cudbear paper violet. When dissolved in water and concentrated, it is very apt to be deposited in silky scales resembling tale in appearance, but the composition of these scales is exactly the same as that of the rhomboidal prism. It would appear from this that it is capable of crystallizing under two distinct forms. Its constituents, determined by a very careful analysis, are as follows:

1 atom phosp	horic	e acid	•	4.5
1 atom soda	•	•	•	4
13 atoms water	r.	•	•.	14.625*
				23.125

23. Octohydrated phosphate of soda. This salt was obtained by Mr. Clarke by dissolving common phosphate of soda and water, and crystallizing it in a calico printer's stove at a tem-



perature of 90°. It constitutes right rhombic prisms, meeting at angles of about 98° and 82°. The figure in the margin represents the most common figure of these crystals, as delineated by Mr. Haidinger. The following

are the measurements of the angles.†

$a  ext{ on } b$ .		•	97°	0'
$a  ext{ on } e$ .	•		128	<b>27</b>
e on $b$ .		•	134	<b>33</b>
a on b.	• ,		128	22
$a  ext{ on } c$ .	•	•	116	<b>42</b>
g on $g$ (over $b$ )	•		117	16
f on $f$ (over $b$ )	•	•	<b>7</b> 8	46
a  on  f	•	•	94	<b>26</b>

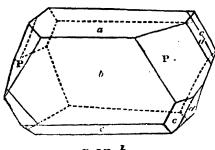
<sup>\* 1</sup> obtained 14.77 water. The surplus (0.145, or about ith atom), was doubtless lodged mechanically between the plates of the crystals.

<sup>†</sup> Brewster's Journal, vii. 315.

This salt does not effloresce when exposed to the air. Its constituents, as determined by Mr. Clarke, are

l atom anhydrous	of soda		8.5		
8 atoms water .	•	•	•	•	9
					17.5*

24. Pyrophosphate of soda. Mr. Clarke observed, that if common phosphate of soda be exposed to a red heat so as to expel all its water of crystallization, and then redissolved in water, and crystallized, the crystals have quite a different form, and the salt possesses new properties. He distinguished the new salt, thus formed, by the name of pyrophosphate of soda.† The crystals of this new salt are small, and do not like those of common phosphate, effloresce when exposed to the air; but remain unaltered. They are transparent, have a vitreous lus-



tre, and a conchoidal fracture. The shape is not easily determined. The figure on the margin represents the different faces, as determined by Mr. Haidinger, who has made the following measurements of the inclination of the various faces to each other.

a on $b$	•		111° 48′
a on $e$ (adjacent)	•		118 22
$b  ext{ on } e$	•		129 50
a on P	•	•	119 36
$a  ext{ on } d$	•	•	123 33
a on $c$			103  24
b on P	•	•	121 43
$\boldsymbol{b}$ on $\boldsymbol{c}$	•		107 30
b on d (over P)	•	•	101 51
	_		

The characteristic property of this salt is, that it precipitates nitrate of silver white, and the precipitate is a neutral phosphate of silver; whereas the common phosphate of soda precipitates nitrate of silver yellow, and in the state of a subsesquiphosphate. Stromeyer has shown that the pyrophosphoric is a weaker acid than the common, which displaces it. By the analysis of Mr. Clarke, this pyrophosphate of soda is composed of

<sup>\*</sup> Brewster's Journal, vii. p. 311. † Ibid. p. 298. ‡ Ibid. p. 314.

l atom anhydrou	s pho	sphat	e of s	oda.	•	•	8.5	Sect. ILL
10 atoms water	•	•	•	•	•	•	11.25	
							10.75*	

Mr. Clarke endeavoured to show that the difference between common and pyrophosphoric acid is, that the common retains about half an atom of water which the pyrophosphoric acid wants. But Stromeyer has shown that both may be made anhydrous without any alteration in their properties.

25. Biphosphate of sodd. This salt may be obtained by adding phosphoric acid to a solution of phosphate of soda till the liquid ceases to precipitate chloride of barium. When the liquid is concentrated and set aside, it gradually deposites crystals of biphosphate of soda. It is very soluble in water, has an acid taste, and reddens vegetable blues. When heated it loses its water and then melts. Mitcherlich found that it crystallizes under two forms incompatible with each other. The most common form is a right rhombic prism, whose faces are inclined at angles of 93° 54′. The other form is a rectangular octahedron. There is always an oblique prism interposed between the two pyramids of the octahedron, the faces of which meet at angles of 78° 30′.+

The constituents of this salt are

2 atoms phosph	oric a	cid	•	•	9
1 atom soda	•	•	•	•	4
4 atoms water	•	•	•	•	4.5
					17.5

- 26. Phosphite of soda is very soluble in water and in absolute alcohol. It crystallizes with difficulty in rhomboids approaching the shape of a cube.
- 27. Hypophosphite of soda. It may be obtained by decomposing hypophosphite of lime by carbonate of soda. When concentrated in the vacuum of an air-pump over sulphuric acid it crystallizes in four-sided tables. They have a pearly lustre, and are deliquescent.
- 28. Arseniate of soda. This salt is best obtained when carbonate of soda is added to an aqueous solution of arsenic acid, till the liquid acquires decided alkaline qualities. When this solution is brought to the requisite degree of concentration, it yields beautiful crystals of arseniate of soda. They are in

<sup>\*</sup> Brewster's Journal, p. 298.

<sup>+</sup> See Ann. de Chim. et de Phys. xix. 412.

oblique rhombic prisms, having precisely the same form as the crystals of phosphate of soda, as was first shown by Professor Mitcherlich.\* When exposed to a dry atmosphere they speedily effloresce and become white on the surface, but do not lose their shape. The taste is cooling, and resembles that of carbonate of soda; but is not so strong. These crystals react slightly as an alkali. Their specific gravity is 1.759. At the temperature of 45° 100 parts of water dissolve 22.268 parts of these crystals. They are insoluble in alcohol, but the surface of a crystal put into that liquid becomes opaque on the surface being deprived of its water of crystallization. When heated it undergoes the watery fusion, and at a red heat the anhydrous salt undergoes the igneous fusion.† The constituents of this salt, according to the analysis of Mitcherlich, are as follows:

1 atom arsenic a	cid	•	•	7.25
1 atom soda	•	•	•	4
$12\frac{1}{2}$ atoms water	•	•	•	14.0625
				<del></del>
				25.3125

But the true quantity of water is doubtless either 12 or 13 atoms. Probably 13; from the analogy of phosphate of soda which contains that quantity.

29. Octohydrated arseniate of soda. This salt was first formed by Dr. Marx of Brunswick, and brought forward by him to show that the arseniates and phosphates of soda have not the same crystalline form. It was subjected to analysis by M. L. Gmelin, who demonstrated that it differs from the preceding arseniate, in containing less water of crystallization.§ I formed it in 1824, and subjected it to analysis; but without attending to the different crystalline form. Mr. Clarke observed the difference between the crystalline shape of these two arseniates, and on analyzing them, found that they differed in their proportions of water. ¶

The shape of the crystals of this salt is precisely the same as that of octahydrated phosphate of soda, as has been determined by Mr. Haidinger. Indeed the two salts resemble each

- \* Ann. de Chim. et de Phys. xix. 387.
- + Annals of Philosophy, xv. 82.
- ‡ In the analysis of this salt which I have given in the Annals of Philosophy, xv. 82, it is obvious that I had inadvertently employed binarseniate instead of arseniate. The two salts were lying side by side in my laboratory, and I had taken up the wrong phial by mistake.
- § Poggendorf's Annalen, iv. 157. || First Principles, ii. 273.
  - ¶ Brewster's Jour. vii. 309.

other so closely, that a minute description of the one would apply perfectly to the other. The mean of two analyses of this salt, by Gmelin, gave

This is equivalent to

Anhydrous salt . 11.25 Water . 8.84

Had the water amounted to 9 instead of 8.84, it would have been exactly 8 atoms. The deficiency amounts to about ½th of an atom. Mr. Clark's analysis gives us

Anhydrous salt . . . 11.25
Water . . . 8.846

which may be considered as identical with the analysis of Gmelin. There can be little doubt that the true constitution of the salt is

30. Binarseniate of soda. This salt may be formed in the same way as the biphosphate of soda. It exactly resembles the second kind of crystalline form which that salt assumes, and its properties so nearly resemble those of that salt, that a minute description is unnecessary. Its constituents are also the same, namely,

2 atoms arsenic acid . . . 14·5
1 atom soda . . . 4
4 atoms water . . . . . . 4·5

31. Biborate of soda or borax. This salt is supposed to have been known to the ancients, and to be the substance denominated chrysocolla by Pliny. At any rate, it is mentioned by Geber as early as the seventh century under the name of borax. Its composition was first pointed out by Geoffroy in 1732, and by Baron in 1748. This salt is brought from the East Indies in an impure state, under the name of tinkal, enveloped in a kind of fatty matter, which Vauquelin has ascertained to be a soap with soda for its base. When purified in Europe, it takes

<sup>\*</sup> See Mitcherlich, Ann. de Chim. et de Phys. xix. 407.

the name of borax. The purification was formerly performed by the Dutch, and of late by the British; but the process which they follow is not known. Valmont Bomare informs us that they extract 80 parts of pure borax from 100 parts of tinkal. The operations are conducted in leaden vessels, and consist chiefly in repeated solutions, filtrations, and crystallizations. Valmont Bomare suspects that they employ lime-water, and Fourcroy has shown that this might be useful in decomposing the soap in which crude borax is enveloped.\*

Borax thus purified may be obtained crystallized in hexangular or octangular prisms, of which two sides are much broader than the remainder. It is of a white colour. Its specific gravity is 1.740.† It converts vegetable blues to green. Its taste is sweetish and alkaline.

It is soluble, according to Wallerius, in 20 times its weight of water of the temperature of 60°, and six times its weight of boiling water.

When exposed to the air it effloresces slowly and slightly. When heated, it swells, loses about four-tenths of its weight, becomes ropy, and then assumes the form of a light porous, and very friable mass, known by the name of calcined borax; in a strong heat it melts into a transparent glass still soluble in water.

When two pieces of borax are struck together in the dark, a flash of light is emitted.

Borax was first accurately analyzed by Arfvedson. Its constituents are

2 atoms boracic a	cid	•	•	6
1 atom soda	•	•	•	4
8 atoms water	•	•	•	9
,				
				10

A great deal of borax is made in Great Britain from boracic acid imported from Tuscany.

32. Octahedral borax. Payen has observed that if a saturated solution of borax at 174° be slowly cooled down, during the time that its temperature is above 103° it deposites crystals which have the form of regular octahedrons. These crystals are composed, according to Payen, of

<sup>\*</sup> Fourcroy, iii. 330.

<sup>†</sup> Kirwan. Wallerius makes it 1.720 (Chemistry, p. 266); Dr. Watson 1.757 (Essays, v. 67.) I found it 1.760.

<sup>‡</sup> Accum, Nicholson's Jour. ii. 28.

2 atoms boracic	acid	•	•	6
l atom soda	•	•		4
4 atoms water	•	•	•	4.5
•				14.5*

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- 33. Sexborate of soda. It has been observed by Wenzel, and more lately by Gmelin, that if 4 atoms of boracic acid be added to a solution of borax containing 2 atoms of acid, the solution when concentrated yields crystals in the form of tables, which have a taste like saltpetre, and do not react as an alkali.† On trying this experiment I did not succeed in destroying the alkaline properties of borax even after adding boracic acid in a still greater proportion than that just stated.
- 34. Silicate of soda. This matter, which possesses the same properties as silicate of potash, is obtained when 2 parts of silica and 5·125 of hydrated soda are fused together in a platinum crucible. It forms a transparent colourless glass, which is soluble in boiling water, and even absorbs moisture from the atmosphere.
- 35. Seleniate of soda. This salt may be obtained by detonating together selenium and nitrate of soda, and dissolving the residue in water. The crystals resemble those of sulphate of soda, and like that salt, it is capable of uniting with various doses of water, and thus altering the shape of its crystals.
- 36. Selenite of soda is very soluble in water, and has the taste of borax. When evaporated to a syrup, it yields small crystalline grains; but cannot be made to crystallize by cooling. When evaporated to dryness, it does not alter in the air. It is insoluble in alcohol.
- 37. Biselenite of soda crystallizes in needles when the solution is sufficiently concentrated. It does not effloresce in the air; but when heated, it first loses its water of crystallization, and then melts into a yellow liquid. On cooling, it becomes white. When heated to redness, one half of the acid flies off in a white smoke, and neutral seleniate remains.
- 38. Quaterselenite of soda, when exposed to spontaneous evaporation, crystallizes in needles.
  - 39. Antimoniate of soda. Both of these salts are soluble in ater. Their properties have not been farther examined.
- 41. Tellurate of soda. Oxide of tellurium dissolves in soda ley, but the properties of the salt have not been examined.

42. Chromate of soda. This is a beautiful transparent yellow salt. Mr. Brooke says that it effloresces very speedily when exposed to the air. I did not perceive this, but my observations on it were made in a damp room which might have prevented the efflorescence. It crystallizes in oblique rhombic prisms. The inclination of the lateral faces to each other is, according to Mr. Brooke's measurement, 80° 4' and 99° 56'. The inclination of the base to the lateral faces is 101° 16'.\* The edges of the prism are often replaced by tangent planes. When heated, it speedily melts in its water of crystallization. It is very soluble in water, but sparingly in alcohol. Its constituents are

1 atom chromic	acid	•	•	6.5
1 atom soda	•	•	•	4
12 atoms water	•	•	•	13.5
				24

43. Bichromate of soda. This salt has a hyacinth red colour, and crystallizes in large irregular plates. It is still more soluble in water than chromate. I analyzed a specimen (not absolutely free from chromate) and found its constituents

2 atoms chromic	e acid	•	•	13
1 atom soda	•	•	•	4
20 atoms water	•	•	•	$22 \cdot 25$
				39.25

- 44. Molybdate of soda. This salt forms large crystals, which effloresce in the air, and are very soluble in water. Acids precipitate from its solution a bimolybdate of soda, which has not hitherto been particularly examined.
- 45. Tungstate of soda. This salt may be obtained by dissolving tungstic acid in a solution of soda. When the solution is evaporated, the tungstate of soda crystallizes in elongated hexahedral plates. I have obtained it also in rhombic flat four-sided prisms. The taste is at first sweet, but it becomes soon intensely bitter. It dissolves in four times its weight of cold water, and in twice its weight of boiling water. Acids from the solution precipitate a bitungstate of soda. I suspect also that a sesquitungstate exists.
- 46. Columbate of soda. When a weak solution of soda in water is digested for some time over hydrated columbic acid,

<sup>\*</sup> Annals of Philosophy (2d series), vi. 287.

and after concentration, is set aside, a number of beautiful crystals in scales, similar in appearance to boracic acid, is deposited. These constitute columbate of soda. They have a silky lustre, an alkaline taste, and render cudbear paper purple. They are soluble in water but not in alcohol. I found the constituents of this salt to be

Columb	ic ac	id .	. •	•	19
Soda	•	. •	•	•	4
Water	•	ĺ	•	•	11.25
					34.25*

47. Manganate of soda. This salt has a red colour, and is

similar in its properties to manganate of potash. Hitherto it has been examined only by Chevillot and Edwards.

48. Oxalate of soda. This salt is easily obtained by saturating oxalic acid with carbonate of soda. It does not crystallize, but is deposited in thin white crusts. When the solution is very dilute it is sometimes deposited in small spherules, rather beautiful, and probably composed of prisms diverging from a centre. It contains no water of crystallization, but usually a little lodged mechanically between the particles of the salt. Its constituents are

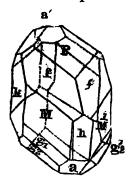
1 atom oxalic a	cid	•	•	4.5
1 atom soda	•	•	•	4
				-
				0.5

49. Binoxalate of soda. When a solution containing 4.5 of oxalic acid is digested on 8.5 of oxalate of soda a complete solution takes place, which, when concentrated, deposites crystals of binoxalate of soda. They have the form of flat rectangular prisms, the larger faces of which are rhomboids with angles of about 120° and 60°. These crystals are not altered by exposure to the air. Their taste is very sour, and they redden vegetable blues. At the temperature of 46°, 100 parts of water dissolve 1.88, and at 83°, 3.49 parts of these crystals. Their specific gravity is 1.980. They are composed of

2 atoms oxalic	acid	•	•	9
l atom soda	•		•	4
3 atoms water	•	•	•	3.375
				16.375

50. Acetate of soda. This salt was discovered by M. Baron, \* First Principles, ii. 76.

and described by him in his Memoir on borax in the year 1747.\* It was formerly known by the absurd name of crystallized foliated earth. It is usually prepared by saturating acetic acid with carbonate of soda, and evaporating the solution till a thin pellicle appears on its surface. When the solution is allowed to cool, the acetate of soda crystallizes in striated prisms, not unlike those of sulphate of soda. It has a sharp taste, approaching to bitter. It is soluble in 2.86 parts of water at the temperature of 60°.+ Its specific gravity is 2.1.† It is



not affected by exposure to the air. When heated, it first loses its water of crystallization, in a strong heat it melts, and in a still stronger its acid is destroyed. The shape of the crystals, as determined by Mr. Brooke, is an oblique rhombic prism. The figure in the margin represents the crystal with all its modifications. The following are the measurements of the angles by Mr. Brooke.

P on M or	$\mathbf{M}'$	•		•	1049	25′
${f P}$ on ${m f}$	•			•	136	nearly
$\mathbf{P}$ on $\boldsymbol{a}$	•	•				<b>35</b>
$\mathbf{M}$ on $\mathbf{M}'$	•			•	84	30
$\mathbf{M}$ on $k$		•		•	137	45
$\mathbf{M}$ on $h$					132	15
$\mathbf{M}$ on $g$ 1	•	•		•		<b>54</b>
$\mathbf{M}  \mathbf{on}  \mathbf{g}  2$	•	•		•	135	<b>50</b>
The constituents of	this	salt b	y	my	analysis	are

T

l atom acetic aci	d	•	•	6.25
1 atom soda		•	•	4
6 atoms water				6.75

- 51. Lactate of soda. This salt does not crystallize. It deliquesces in the air, and is very soluble in water and alcohol.
- 52. Formate of soda. This salt crystallizes in flat four-sided prisms. Its taste is saltish and bitter. Soluble in twice its weight of cold water. When heated it undergoes the watery fusion, and may be afterwards reduced by heat to a dry powder. Its constituents, as determined by Göbel, are

<sup>\*</sup> Mem. Scavans Etrang. i. 326. + Bergman, v. 78.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

<sup>§</sup> Annals of Philosophy (2d series), vi. 39.



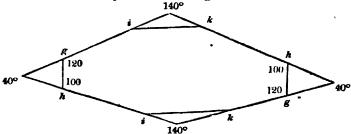
1 atom formi	c acid	•	•	4.625
l atom soda	•	•	•	4
2 atoms water	er .	•	•	$2 \cdot 25$
				<del></del>
				10.075*

53. Mellate of soda. This salt crystallizes in fine silky needles, of which it has been hitherto impossible to determine the shape.+

54. Tartrate of soda. This salt crystallizes in four-sided prisms, rather oblique, and usually terminated by bihedral sum-Or it may be obtained in fine needles. It is not altered by exposure to the air, but when gently heated falls to powder. According to Wenzel it dissolves in its own weight of cold water. ‡ Hot water dissolves it in any quantity. It is insoluble in absolute alcohol. Its constituents, by my analysis, are

1	atom tartaric	acid	•	•	8.25
1	atom soda	•	•	•	4
2	atoms water	•	•	•	2.25
					14.5

55. Bitartrate of soda. This salt is formed by dissolving the preceding in eight times its weight of boiling water, and adding half the weight of the salt of tartaric acid to the solution. On concentrating the liquid, and setting it aside, small crystals of bitartrate of soda are deposited. They have usually the form of six-sided prisms, two of the angles of which are (according to Ecken) of 140°, two of  $101^{\circ}\frac{1}{2}$ , and two of 120°. It is probable from this that the primary form is a right rhombic prism. the faces of which meet at angles of  $101^{\circ}\frac{1}{0}$  and  $78^{\circ}\frac{1}{0}$ . Bucholz considers it as a rhombic prism with angles of 40° 140°. The base of which may be thus represented.



The lines i k and g h represent the faces which replace the

<sup>\*</sup> Schweigger's Jour. xxxii. 345; and Gehlen's Jour. ii. 42. Gilbert's Annalen, xv. 470.

<sup>+</sup> Wöhler, Poggendorf's Annalen, vii. 332. 1 Wervandtschaft, p. 308. 2 н II.

edges and render the prism six or eight-sided. Taste very sour. It is soluble in 9 times its weight of cold, and in 1.8 of boiling water. Insoluble in absolute alcohol. Its constituents, according to the analysis of Bucholz, are

2 atoms tartaric a	icid	•	•	16.5
l atom soda		•	•	4
3 atoms water	•		•	3.375
				02.075

- 56. Vinate of soda. Transparent crystals consisting of four and six-sided prisms, not altered by exposure to the air, and which lose no heat when exposed to the temperature of 212°. Easily soluble in water. The solution undergoes spontaneous decomposition.+
- 57. Pyrotartrate of soda. Does not crystallize regularly. Deliquesces in the air.
- 58. Citrate of soda. This salt may be formed by the same process as the tartrate of soda. By proper evaporation it is obtained crystallized in six-sided prisms, not terminated by pyramids. Its taste is salt and cooling, but mild. It is soluble in 12 parts of water. When exposed to the air, it effloresces slightly. When heated, it melts, swells, bubbles up, blackens, and is decomposed.
- 59. Malate of soda. A deliquescent, very soluble, incrystallizable salt. The bimalate forms permanent crystals soluble in water; but insoluble in alcohol.§
- 60. Fungate of soda. Does not crystallize. Dissolves easily in water, but is not soluble in alcohol.
- 61. Mucate of soda. Right rectangular prisms with square bases. White and transparent, tough, taste slightly saline, and like that of phosphate of soda. Not very soluble in water. A very moderate heat gives it a brown colour. Its constituents, by my analysis, are

1 atom mucic aci	$\mathbf{d}$	•	•	13
1 atom soda	•		•	4
5 atoms water	•	•	•	5.625
				22.625

62. Pyromucate of soda. Crystallizes with difficulty. Does not deliquesce. Less soluble in alcohol than pyromucate of potash.

\* Bucholz, Gehlen's Jour. v. 520. † Walchner. ‡ Rose. § Donovan. | Braconnot.

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63. Succinate of soda. When pure succinic acid is saturated with soda, the solution by spontaneous evaporation yields beautiful transparent crystals of succinate of soda; some of which are four-sided prisms with dihedral summits; others six-sided prisms, terminated by an oblique face.\* This salt has a bitter taste, is less soluble in water than common salt, and does not deliquesce when exposed to the air. Its constituents, by my analysis, are

1 atom succinic ac	id	•	•	6.25
1 atom soda	١.	•		4
6 atoms water	•	•	•	6.75

17

This is exactly the composition and atomic weight of acetate of soda.

- 64. Benzoate of soda. The crystals of this salt are larger, but its taste is the same with that of benzoate of potash. It is very soluble in water. It effloresces in the air. Its taste is sweetish and sharp. Scarcely soluble even in boiling alcohol.
- 65. Gallate of soda. An irregular crystalline mass, hardly examined.
- 66. Kinate of soda. It crystallizes in beautiful six-sided prisms, which undergo no alteration by exposure to the air. Exposure to the heat of 212° does not sensibly diminish their weight. It is probable from this that it contains no water of crystallization.†
- 67. Meconate of soda. It may be formed by dropping a solution of glauber salt into liquid meconate of barytes as long as a precipitate continues to fall. The filtered liquid when concentrated deposites small granular crystals, which, according to John, effloresce in the air, and are soluble in five times their weight of water. They are composed, according to Choulant, of

Meconic a	acid	•	•	32
Soda	•		•	40
Water	•	•	•	28
				700

- 68. Bimeconate of soda. Crystalline grains, reddening vegetable blues, easily soluble in water, but scarcely in alcohol.
- 69. Camphorate of soda. This salt may be formed in the same way as the camphorate of potash. When concentrated

<sup>\*</sup> Morveau, Ann. de Chim. xxix. 166.

<sup>†</sup> Henry and Plisson, Ann. de Chim. et de Phys. xli: 328.

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to the thickness of a syrup, some prismatic crystals make their appearance. This salt speedily deliquesces when exposed to a moist atmosphere. It is not soluble in water. 100 parts of absolute alcohol dissolve 1.25 parts of this salt at the temperature of 45°. When heated it melts, and is decomposed when the temperature is raised.\*

70. Suberate of soda. It may be obtained by saturating suberic acid with carbonate of soda. It shoots into transparent needles and four-sided prisms. Its taste is saltish and bitter. It dissolves in its own weight of cold water, and is still more soluble in hot water. It is soluble also in alcohol. When exposed to the air it absorbs moisture.

71. Stearate of soda. To obtain this salt let 20 parts of stearic acid be put into a flask with 200 of water and 13 of soda, and digested. The combination takes place, and the salt separates from the liquid in clots. Let it be dried, and then pressed between folds of blotting paper. When dry let it be dissolved in 25 times its weight of boiling alcohol. On cooling the liquid becomes gelatinous, and by degrees pure stearate of soda appears in the form of brilliant crystals. Collect them on a filter, wash them with cold alcohol, and then allow them to dry.

The crystals are semitransparent plates; they are at first tasteless; but leave an alkaline impression in the mouth. They dissolve in 20 times their weight of boiling alcohol, of the specific gravity 0.821. The solution becomes muddy at about the temperature of 158°. It assumes the form of a jelly, which by degrees diminishes in bulk, and is converted into crystals. It is insoluble in water, and very slightly soluble in ether. It contains no water, but is composed of

1 atom stearic acid, 1 atom soda.

72. Bistearate of soda. We obtain this salt by digesting 1 part of stearate of soda in 2000 parts of water. The liquid takes up one-half of the soda, and the portion remaining undissolved is bistearate. It is more fusible than the stearate; and is white, insipid, and without colour. It is insoluble in water, but very soluble in alcohol, and the solution reddens infusion of litmus; but the blue colour is restored by adding water to the liquid.§

73. Margarate of soda. This salt has the form of small semitransparent plates, at first tasteless; but it leaves an alka-

<sup>\*</sup> Brandes, Schweigger's Jour. xxxviii. 285.

<sup>†</sup> Ibid. xxxiii. 83.

<sup>‡</sup> Chevreul, sur les corps gras, p. 50.

<sup>§</sup> Ibid. p. 53.

line impression in the mouth. It is soluble in about 50 times its weight of boiling alcohol. It is insoluble in water.\*

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- 74. Bimargarate of soda. Obtained by digesting margarate of soda in a great quantity of water. It is white, insipid, destitute of smell, more fusible than margarate, insoluble in water, but very soluble in alcohol.†
- 75. Ricinate of soda. Similar in its properties to ricinate of potash.
- 76. Oleate of soda. Put into a flask 1 part of oleic acid; 0.66 of hydrate of soda, dissolved in 5 parts of water, digest for some time, and then allow the whole to cool. separates in a mass much harder and firmer than oleate of potash. Reduce it to powder, press it between the folds of blotting paper, and, finally, dissolve it in 10 times its weight of boiling alcohol, of the specific gravity 0.821. It separates in a solid mass, when the solution cools, or is properly concentrated. It is semitransparent, without smell, and has a bitter and alkaline taste. It absorbs moisture from the atmosphere, but does not deliquesce. It dissolves at 50° in ten times its weight of water. It dissolves also in 10 times its weight of boiling alcohol of 0.821. Ether has very little action on it.1
  - 77. Binoleate of soda exists; but has not been examined.
- 78. Phocenate of soda. Obtained by neutralizing carbonate of soda, dissolved in water with an excess of phocenic acid, and evaporating to dryness. When dissolved in water, and concentrated and exposed in a very dry atmosphere, it crystallizes. The crystals resemble cauliflower, and deliquesce in a moist atmosphere.
- 79. Butyrate of soda. Prepared in the same way as butyrate of potash. It resembles that salt, but is less deliquescent.
- 80. Caproate of soda. Prepared in the same way as caproate of potash, which it resembles. A concentrated solution of it, when exposed to the air, is converted into a white mass.¶
- 81. Cholesterate of soda. Brownish yellow, not crystallizable, deliquescent. Insoluble in alcohol and ether.
  - 82. Pinate of soda. Similar to the same salts of potash.
- 84. Carbazotate of soda. Crystallizes in fine silky needles of a light yellow colour. It dissolves in about 20 times its

<sup>\*</sup> Chevreul, sur les corps gras, p. 65. † Ibid. p. 66. ‡ Ibid. p. 88. § Ibid. p. 111. || Ibid. p. 127. ¶ Ibid. p. 141.

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weight of water at 60°. In other respects it agrees with carbazotate of potash.\*

- 85. Urate of soda. A white powder having the same appearance as pure uric acid. Soluble in soda ley.
- 86. Pyrurate of soda. A salt soluble in water; but seemingly not crystallizable.+
- 87. Aspartate of soda. Crystallizes easily, and is characterized by an odour of beef tea, agreeably saline.
- 88. Hydrocarbosulphate of soda. This salt crystallizes with more difficulty, and in quite a different form from that of hydrocarbosulphate of potash. It deliquesces in moist air, and is not separated from its solution in alcohol by sulphuric ether.§
- 89. Sulphovinate of soda. It forms brilliant crystals, whose form is irregular, and effloresces in the atmosphere. || They consist of transparent six-sided tables. The taste is sweet. When thrown into a red hot platinum crucible they burn with flame.
- 90. Sulphonaphthalate of soda. It resembles sulphonaphthalate of potash. The crystals are white, pearly, and unaltered in the air. They have a decided metallic taste.\*\*
- 91. Sinapate of soda. When the solution of this salt is left to spontaneous evaporation, it shoots into small crystalline grains.

## SECTION IV. -- SALTS OF LITHIA.

The salts of lithia have been hitherto but superficially examined, owing to the difficulty of procuring their base in sufficient quantity.

Characters.

- 1. They are all soluble in water (as far as is known), and in this respect resemble the salts of potash and soda. But the carbonate of lithia is much less soluble than the carbonates of potash or soda.
- 2. When carbonate of potash is dropped into a concentrated solution of a salt of lithia, a white precipitate falls. This precipitate may be redissolved again by diluting the liquid with a
  - \* Liebig, Ann. de Chim. et de Phys. xxxv. 83.
  - † Chevallier and Lassaigne, Ann. de Chim. et de Phys. xiii. 160.
  - ‡ Plesson, Ibid. xl. 314.
  - § Zeise, Annals of Philosophy (2d series), iv. 244.
  - || Vogel, Ann. de Chim. et de Phys. xiii. 73.
  - ¶ Vogel, Gilbert's Annalen, lxiii. 94.
  - \*\* Faraday, Annals of Philosophy (2d series), xii. 207.

3. Muriate of platinum occasions no precipitate when dropped into a salt of lithia.

4. Several of the salts of lithia melt at a very low tem-

perature.

- 5. When the salts of lithia are heated to redness in a platinum vessel, they act with considerable energy upon that metal.
- 6. Neither prussiate of potash, nor infusion of nut-galls, occasions any precipitate in the salts of lithia.
  - 7. Salts of lithia are not precipitated by caustic potash.
- 8. If to a salt of lithia we add a quantity of phosphate of soda, and evaporate, the solution becomes muddy. If we evaporate to dryness, and pour water on the residue, a white powder remains undissolved, which falls slowly to the bottom of the vessel.
- 9. When an alcoholic solution of a lithia salt is kindled, it burns with a purple red colour.
- 10. If we mix together 1 part of fluor spar, and  $1\frac{1}{2}$  part of sulphate of ammonia, and add to the mixture a little of a lithia salt, and heat before the blowpipe, the flame has at first a green colour; but when the mixture fuses, the colour of the flame becomes purple red.\*
- 1. Sulphate of lithia. This salt crystallizes in small four-sided crystals, whose bases, according to Vauquelin, are squares. Its taste is saline, without any of the bitterness which distinguishes the sulphates of potash and soda. It requires a strong red heat to fuse it, but the presence of a little gypsum makes it fusible below a red heat. It is scarcely altered by exposure to the air. Its constituents are

1 atom sulphuric acid . 5
1 atom lithia . . . 1.75
1 atom water . . . . 1.125

7.875

- 2. Bisulphate of lithia dissolves in water more readily than the sulphate. It crystallizes in six-sided tables. When exposed to a very high temperature, sulphurous acid and oxygen gas are driven off, and sulphate of lithia remains behind.+
  - 3. Nitrate of lithia. This salt is colourless, very soluble in

<sup>\*</sup> Turner. † Gmelin, Gilbert's Annalen, lxii. 409.

water, and crystallizes in four-sided prisms, with rhomboidal bases. Its taste is very sharp. It very speedily deliquesces when exposed to the air. It melts when exposed to a very moderate degree of heat, and runs into a liquid. It dissolves readily in alcohol.\*

4. Carbonate of lithia. When this salt is obtained by precipitating a concentrated salt of lithia by means of carbonate of potash, it is a white powder, having a strong alkaline taste, and soluble in about 100 times its weight of cold water; but more soluble in hot water. It melts when heated to redness, and assumes on cooling the appearance of enamel. When heated in a platinum crucible, the metal is always strongly attacked. The carbonates of the other alkalies, on the other hand, restore the metallic lustre to this metal when tarnished. It is insoluble in alcohol. Its constituents are

1 ator	n carbon	ic aci	.d	•	2.75
1 ator	n lithia	•	•	•	1.75
					4.5

- 5. Bicarbonate of lithia. When a current of carbonic acid gas is passed through water in which carbonate of lithia is suspended, a portion is dissolved doubtless in the state of bicarbonate. By spontaneous evaporation a crystalline crust is obtained, which decrepitates strongly when heated. This salt is said to occur in some mineral waters in Bohemia.
- 6. Phosphate of lithia. This salt falls in the state of a white insoluble powder, when phosphate of ammonia is dropt into a solution of sulphate of lithia. But phosphoric acid does not occasion a precipitate when dropt into that salt, nor when dropt into carbonate of lithia. But if heat be applied to the carbonate after the addition of phosphoric acid, carbonic acid is disengaged, and phosphate of lithia falls down.
- 7. Biphosphate of lithia. When we dissolve the preceding salt in phosphoric acid, we obtain a biphosphate, which crystallizes when left to spontaneous evaporation. It is very soluble in water.
- 8. Borate of lithia. This acid combines in two proportions with lithia. The neutral borate may be made by boiling together the aqueous solutions of boracic acid, and carbonate of lithia. The combination takes place very slowly. The

<sup>\*</sup> Arfvedson, Ann. de Chim. et de Phys. x. Gmelin, Gilbert's Annalen, lxii. 410.

<sup>#</sup> Gmelin, Gilbert's Annalen, lxii. 400.

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borate of lithia is very soluble in water, and when the solution is evaporated sufficiently, a gummy transparent matter remains, which deliquesces when left exposed to the air.

Biborate of lithia is capable of crystallizing, and is much less soluble than the borate of lithia, though more so than boracic acid.\*

- 9. Selenite of lithia. Deliquesces in the air, fuses below a red heat into a yellow liquid, which on cooling concretes into a crystalline mass, which is translucent, has a pearly lustre, and is composed of large plates.
- 10. Chromate of lithia. This salt has a yellow colour, and crystallizes in parallelopipeds with rhomboidal bases. It is readily soluble in water.†
- 11. Oxalate of lithia. This salt may be obtained by saturating oxalic acid with carbonate of lithia. It crystallizes with difficulty, and dissolves readily in water.‡ Binoxalate of lithia crystallizes and dissolves readily in water.
- 12. Acetate of lithia. This salt may be obtained by dissolving carbonate of lithia in acetic acid, with the assistance of heat. When evaporated, it leaves a gummy matter which speedily deliquesces, and in the deliquesced mass, crystalline plates gradually make their appearance.
- 13. Tartrate of lithia. This salt dissolves readily in water, and does not crystallize, but forms a white opaque matter which does not deliquesce when exposed to the air. The bitartrate, on the contrary, crystallizes readily, and is not so soluble as the tartrate.
- 14. Mucate of lithia. Mucic acid readily dissolves carbonate of lithia, and yields when slowly evaporated small crystals of mucate of lithia, which effloresce when exposed to the air, and dissolve with facility in water.¶
- 15. Malate of lithia. Malic acid extracted from the berries of the mountain ash dissolves carbonate of lithia with facility; but the solution scarcely yields crystals. When evaporated, a syrupy mass remains which cannot be easily dried.\*\*
- 16. Benzoate of lithia. Benzoic acid readily decomposes carbonate of lithia, and forms a salt which dissolves easily in water, and does not crystallize, but leaves a white opaque matter which deliquesces in the air. When heated to redness, it is converted into carbonate of lithia, which leaves when dissolved in water, a very bulky coal.++
  - \* Gmelin, Gilbert's Annalen, lxii. 412. † Ibid. 413. ‡ Ibid. 414. § Ibid. 415. ¶ Ibid. ¶ Ibid. 416. \*\* Ibid. +† Ibid.

17. Gallate of lithia. Gallic acid readily dissolves carbonate of lithia. The solution has a dark green colour, and when evaporated, leaves a black matter behind, which does not yield crystals.\*

## SECT. V .- SALTS OF BARYTES.

A considerable number of the salts of barytes are insoluble in water.

Characters.

- 1. They are white or transparent, and in general affect a crystalline form.
- 2. If a little of the solution of sulphate of soda be let fall into a salt of barytes, a white powder immediately precipitates, which is insoluble in nitric acid.
- 3. When heat is applied to a salt of barytes, it is not completely dissipated. If the acid be combustible, carbonate of barytes remains behind; if the acid be not combustible or volatile, the salt remains behind undecomposed.
- 4. Prussiate of potash occasions no precipitate in a salt of barytes; unless the acid happens to contain a metallic basis. The same remark applies to hydrosulphuret of potash when dropped into a salt of barytes.
  - 5. Most of the salts of barytes are poisonous.
- 6. When a fusible salt of barytes is heated before the blowpipe, it tinges the flame yellow. The same change of colour is produced when alcohol, containing any soluble salt of barytes in solution, is burnt.
- 7. Oxalate of ammonia, when dropt into a solution of a barytes salt, does not occasion an immediate precipitate.
- 1. Sulphate of barytes. This mineral occurs in considerable quantity, chiefly in veins, and very frequently accompanies galena and grey copper ore. Its nature was first ascertained by Assessor Gahn. It often occurs crystallized, and the primary form is a right rhombic prism, the faces of which are inclined at angles of 101° 42′ and 78° 18′. It cannot be crystallized by art. This salt is insoluble in water, or at least only soluble in 43000 times it weight of water at the temperature of the atmosphere.† Sulphuric acid dissolves it when concentrated and boiling, but it is precipitated by the addition of water.‡
  - \* Gmelin, Gilbert's Annalen, lix. p. 415. † Kirwan's Min. i. 136.
- † Thus it forms a kind of supersulphate, capable of crystallizing, as Withering first observed. Mr. Hume has also mentioned it in Phil. Mag. xiv. 357. The fact was well known to chemists. This solution, however,

When suddenly heated, it breaks in pieces and flies about with a crackling noise. This phenomenon, which is called decrepitation, is occasioned by the sudden conversion of the water which it contains into steam. When heated very violently it melts, and before the blow-pipe is converted into a white opaque globule. According to Saussure, a heat equal to 35° Wedgewood is required to fuse it.\* When formed into a thin cake with flour and water, and heated to redness, it phosphoresces in the dark. This was first observed in a variety of this substance known by the name of Bologna stone. Lemery informs us, that the property was discovered by an Italian shoemaker named Vincenzo Casciarolo. This man found a Bologna stone at the foot of Mount Paterno, and its brightness and gravity made him suppose that it contained silver. Having exposed it to the fire, doubtless in order to extract from it the precious metal, he observed that it was luminous in the dark. Struck with the discovery, he repeated the experiment, and it constantly succeeded with him. It is evident that by the calcination it must be converted, at least partly, into sulphuret. I found that when sulphate of barytes was obtained by precipitation, and after being well washed was dried by simple exposure to the air in a damp room, it retained 3 per cent. of water lodged mechanically in its pores. The constituents of this salt are

1 atom	of sulphuric	acid	•	•	5
1 atom	barytes	•	•	•	9.5
					14.5

2. Sulphite of barytes. A tasteless white powder, insoluble in water. When heated it gives off sulphur. It dissolves in aqueous sulphurous acid, and crystallizes in needles. Its constituents are

1 atom	sulphurous acid		•	•	4
1 atom	barytes .	•	•	•	9.5
					13.5

It contains about 2 per cent. of water lodged mechanically in the pores of the salt.

3. Hyposulphite of barytes. This salt may be obtained by

is but very imperfectly entitled to the name of supersulphate of barytes; as it parts with its excess of acid at a moderate heat, which by no means is the case with supersulphate of potash.

<sup>\*</sup> Jour. de Phys. xlv. 15.

pouring muriate of barytes into a concentrated solution of hyposulphite of lime. It falls in the state of a white brilliant scaly powder. It is very slightly soluble in water. When the muriate of barytes is poured into dilute hyposulphite of lime, no precipitate appears at first, but small crystalline grains gradually fall, speedily followed on brisk agitation by a copious separation of the barytes salt. Mr. Herschell, to whom we are indebted for every thing at present known concerning this salt, considers it to be a bihyposulphite.\* Hence its constituents must be

Acid	•	•	•	10
Barytes	•	•	•	9.5
				19.5

4. Bihydrated hyposulphate of barytes. This salt is obtained when hyposulphate of manganese is digested over barytes. The oxide of manganese, and all the sulphuric acid, is separated, and the liquid contains only a solution of hyposulphate of barytes. By evaporation the salt may be obtained in crystals, by keeping the liquid for some time in a hot place.

The crystals are usually four-sided prisms, deviating only 6° 45′ from a right angle by Dr. Heeren's measurement. They are terminated by irregular four-sided pyramids, the faces of which are set on the edges. There is another variety of crystallization, with faces usually convex, and not easily described.† It is not altered by exposure to the air. When heated it strongly decrepitates. It dissolves in 1·1 times its weight of boiling water; in 4·04 times its weight at 64°, and in 7·17 times its weight at 47°. It is insoluble in alcohol. When strongly heated, water and sulphurous acid are driven off, and sulphate of barytes remains. Its constituents, as determined by Gay-Lussac and Welter, with which the analysis of Heeren agrees, are

1 atom hyposulph	iuric e	icid	•		9
1 atom barytes	•	•	•	•	9.5
2 atoms water	•	. •	•	•	2.25
					20.75

- 5. Quater hydrated hyposulphate of barytes. When a solution of hyposulphate of barytes is set aside in a temperature not
  - \* Edin. Philos. Journ. i. 20.

<sup>†</sup> Figures of both these crystals have been given by Heeren in Poggendorf's Annalen, vii. 173. The figures are in Tab. 11, figs. 4, 5, 6.

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exceeding 41°, crystals are gradually deposited, containing twice as much water as the preceding salt. The crystals are large, and are in four-sided prisms, terminated by four-sided pyramids, approaching very nearly to the shape of sulphate of barytes. The inclination of the faces of the prism, measured by a common goniometer, are 102° and 78°.\* When heated it decrepitates strongly, but does not melt, but is converted into sulphate of barytes without altering its shape. Its constituents, as determined by Heeren, are

1 atom hyposulph	uric a	cid	•	•	9
1 atom barytes	•	•	•	•	9.5
4 atoms water	•	•	•	•	4.5
			•		93

6. Nitrate of barytes. This salt was formed immediately after the discovery of barytes. Vauquelin has added considerably to our knowledge of its properties. It is usually prepared by dissolving native carbonate of barytes in nitric acid, or by decomposing sulphuret of barytes by means of nitric acid, and evaporating the filtered solution till the nitrate crystallizes.

Its crystals are regular octahedrons, sometimes cubes, and often they adhere to each other in the form of stars. The summits of the pyramids are often truncated. Sometimes it crystallizes in three-sided tables with the angles truncated. Sometimes it is obtained in small brilliant plates. Its specific gravity is 2.9149.† It is very easily reduced to powder.

Its taste is hot, acrid, and austere. 100 parts of water at

Its taste is hot, acrid, and austere. 100 parts of water at 32° dissolve 5 parts of it; at 58°, 15.8 parts; and 120°, 17 parts; and at 215°, 35.2 parts of this salt, according to the determination of Gay-Lussac. It contains no water, but is a compound of

1 atom nitric acid	•	•	6.75
1 atom barytes	•	•	9.5
	•		
			16.95

It is insoluble in alcohol of the specific gravity 0.800. It is but little altered by exposure to the air. When thrown on burning coals it decrepitates, undergoes a kind of fusion, and then becomes dry. When strongly heated in a crucible, the whole

<sup>\*</sup> See a description and figure of the crystal by Heeren, in Poggendorf's Annalen, vii. 176. He considers the primary form an octahedron, but we might also assume a right rhombic prism with angles of 98° and 102°.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

of the acid is gradually driven off, and the barytes remains pure. It detonates less violently with combustibles than most of the other nitrates.

7. Chlorate of barytes. The best method of obtaining the chlorate of barytes is to pour warm water on a quantity of the earth procured by Vauquelin's method, and to pass a current of gas through this mixture kept warm. By this method the usual mixture of chloride and chlorate is obtained. Now these two salts, when barytes is their base, possess the same degree of solubility, and resemble each other in the form of their crystals, so that they cannot be obtained separate by repeated crystallizations. Mr. Chenevix succeeded by the following ingenious method: Phosphate of silver, when boiled in solutions of the earthy chlorides has the property of decomposing them; the phosphoric acid combines with the earth, and the chlorine with the silver. But this salt produces no such change on the earthy chlorates. Now both the phosphate of barytes and the chloride of silver are insoluble in water. Of course, when phosphate of silver is boiled in a solution of chloride and chlorate of barytes, the whole muriate is decomposed into chloride of silver and phosphate of barytes, which are insoluble, and the only substance which remains in solution is chlorate of barytes.

It crystallizes in square prisms, terminated by an oblique face. Its taste is sharp and austere. It dissolves in about four times its weight of cold water. The solution is neither precipitated by nitrate of silver nor muriatic acid. This salt is insoluble in alcohol. When heated, it loses 39 per cent. of its weight, owing to the escape of oxygen gas. The residue possesses alkaline properties.\* From the analysis of this salt by Chenevix, its constituents are

1 atom chloric acid	•	•	$9 \cdot 5$
1 atom barytes	•	•	$9 \cdot 5$
2 atoms water	•	•	2.25
			21.25

8. Bromate of barytes. This salt forms acicular crystals, soluble in boiling water, but little soluble in cold water. On burning coals it fuses with a green flame.† It has not been analyzed, but is doubtless a compound of

<sup>\*</sup> Vauquelin, Ann. de Chim. lxv. 100.

<sup>†</sup> Balard, Ann. de Chim. et de Phys. xxxii. 367.

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1 atom bromic acid	•	•	15
1 atom barytes	•	•	9.5

24.5

9. Iodate of barytes. This salt may be formed by mixing a salt with base of barytes, with iodate of potash. It precipitates in powder and becomes farinaceous in drying. It cannot be deprived of the whole of its water by exposure to a temperature equal to that of boiling water. When heated sufficiently it is decomposed into oxygen, iodine, and barytes. One hundred parts of boiling water dissolve 1.06 of this salt; 100 parts of water at 63°½ dissolve only 0.03 of it. On burning coals it does not fuse and scarcely deflagrates.\* Its constituents are

1 atom iodic acid	l .	•	20.75
1 atom barytes	•	•	9.5
			30.25

10. Carbonate of barytes. This salt seems first to have been examined by Bergman. Withering first found it native in 1783. Hence it has received the name of Witherite. Since that time it has been examined by Kirwan, Klaproth, Hope, Pelletier, Fourcroy, Vauquelin, and Berzelius, and its properties described with great precision. It may be prepared artificially by exposing barytes water to the open air, or by passing carbonic acid gas into it. In either case the carbonate precipitates in the state of a white powder. It occurs native in considerable quantity in veins along with lead ore in different parts of England. The abandoned lead mine at Anglesark in Yorkshire, seems to have yielded it in very large quantity. It occurs also near Neuberg in Stiria, in irregular beds. Other localities are mentioned in Hungary, Sicily, Siberia, &c., but in these it seems to occur only sparingly.

It is occasionally crystallized, and the primary form is a right rhombic prism with angles of 118° 30′ and 61° 30′, as measured by Mr. W. Phillips. The usual crystal is a six-sided prism, probably formed by the intersection of three of the primary crystals. It has no sensible taste; yet it is poisonous. Its specific gravity, when native, is 4.331; when prepared artificially, it scarcely exceeds 3.763.

Cold water dissolves  $\frac{1}{4304}$  part, and boiling water  $\frac{1}{2304}$  part of this salt. It is not altered by exposure to the air. It is

<sup>\*</sup> Gay-Lussac, Ann. de Chim. xci. 81.

decomposed by the application of a very violent heat,\* either in a black lead crucible, or when formed into a paste with charcoal powder. Its constituents are

1 atom carbonic acid	•	•	2.75
1 atom barytes .	•	•	9.5
			10.05

- 11. Bicarbonate of barytes. Fourcroy informs us that when a current of carbonic acid is passed through water, in which carbonate of barytes is mechanically mixed, the liquid dissolves  $\frac{1}{830}$ th part of its weight of the salt. This dissolved portion is evidently in the state of a bicarbonate. It appears also from the experiments of Berthollet and Longchamp, that when a solution of a barytes salt is mixed with one of bicarbonate of potash or soda, a double decomposition takes place, and a portion of the bicarbonate of barytes remains in solution. But this salt cannot be obtained in a dry state.
- 12. Croconate of barytes. When croconate of potash, and chloride of barium are mixed, a light yellow powder falls, which is croconate of barytes.
- 13. Phosphate of barytes. This salt may be obtained by dropping neutral phosphate of ammonia into a neutral salt of barytes. Care must be taken to add the phosphate slowly and in drops. For if too much be poured in biphosphate of barytes is formed, and thus a mixture of two salts precipitates.

This salt is tasteless, uncrystallizable by art, insoluble in water, and not altered by exposure to the air. Its specific gravity is 1.2867.‡ When strongly heated it melts into a gray-coloured enamel. Its constituents are

1 atom phosphoric	acid	•	•	4.5
1 atom barytes	•	•	•	9.5
				14

14. Biphosphate of barytes. This salt is obtained when phosphate of barytes is dissolved in phosphoric acid, till the liquid refused to take up any more. The solution being evaporated spontaneously deposited white crystals, which when separated from the liquid resembled crystals of muriate of barytes. They contain water of crystallization. They have a taste similar to that of the muriate, but at the same time acid. This salt reddens vegetable blues. When heated sufficiently it swells into

<sup>\*</sup> Dr. Hope. + L. Gmelin. ‡ Hassenfratz, Ann. de Chim. xxviii. 12.

a porous mass like burnt alum. Water decomposes this salt, by dissolving the excess of acid. It contains exactly twice as much acid as the neutral phosphate; or it is composed of two atoms acid + one atom barytes.\* Its constituents, as determined by Berzelius, are

2 atoms phosphoric aci	d	•	•	9
1 atom barytes	•	•	•	9.5
2 atoms water	•	•	•	2.25
			•	20.75

15. Sesquiphosphate of barytes. This salt is obtained when a solution of the preceding salt is poured into alcohol. A bulky precipitate falls. When dried it is a light, white, tasteless powder. It is composed of  $l\frac{1}{2}$  atom acid + 1 atom of barytes, or, which comes to the same thing, of 3 atoms acid + 2 atoms barytes.+

Berzelius found that when neutral phosphate of barytes is digested in liquid ammonia, a portion of the acid is removed, and a salt remains, which he found composed of

1 atom phosphoric acid,  $1\frac{1}{4}$  atom barytes.‡

The probability is, that in this case one-fourth part of the salt loses the half of its acid, and is converted into diphosphate, which, by combining with the remaining portion of salt, prevents the decomposition from going farther. The new salt obtained then would seem to be a compound of

	Acid.	Barytes.
1 atom diphosphate of barytes 3 atoms phosphate of barytes		+ 2 atoms + 3
•	<del></del>	<del></del> + 5

For it is obvious that 4 atoms acid and 5 atoms base are in the same ratio as 1 atom acid and  $1\frac{1}{4}$  atom base. It would seem from this that a diphosphate of barytes exists.

16. Phosphite of barytes. Berzelius prepared this salt by pouring muriate of barytes into a solution of phosphite of ammonia. No precipitate appeared at first; but in 24 hours the glass was covered with a crust of phosphite of barytes. When washed and dried, its composition, according to the experiments of Berzelius, was

<sup>\*</sup> Berzelius, Ann. de Chim. et Phys. ii. 154. † Ibid. p. 156.

<sup>†</sup> Ann. de Chim. et de Phys. xi, 114.

Ciass I.	- !	<ul><li>l atom phosphorous</li><li>l atom barytes</li><li>l atom water</li></ul>	acid	•	•	3·5 9·5 1·125
						14.125

When heated the water is decomposed, and converts the phosphorous into phosphoric acid. The gas given out is almost pure hydrogen. It burns with a blue flame, and scarcely affects the solution of nitrate of silver.\*

17. Biphosphite of barytes. This salt was obtained by M. H. Rose, by digesting the preceding salt in a solution of phosphorous acid. When the solution is concentrated sufficiently in vacuo over sulphuric acid, it crystallizes in small grains, whose shape cannot be made out. It is not very soluble in water, and yet it attracts moisture from the atmosphere. When heated it gives out subphosphuretted hydrogen gas. Its constituents, as determined by H. Rose, are

<b>2</b>	atoms phospho	orou	s acid	•	7
1	atom barytes	•	•	•	9.5
$2\frac{1}{2}$	atoms water	•	•	•	2.8125
				4	

19.3125+

- 18. Diphosphite of barytes. It is said by Dulong that phosphite of barytes is slightly soluble in water, and that when the solution is strongly heated, pearly scales fall to the bottom, which constitute diphosphite of barytes.
- 19. Hypophosphite of barytes. A very soluble salt, which crystallizes with difficulty.‡
- 20. Arseniate of barytes. This salt precipitates in small white crystalline plates, when arseniate of soda is dropt into a solution of chloride of barytes. It is tasteless, and insoluble in water. Its constituents, according to Berzelius, are

1 atom arsenic acid		•	7.25
1 atom barytes	•	•	9.5
2 atoms water	•	•	2.25
*			700

19.0

21. Binarseniate of barytes. This salt may be obtained by digesting arseniate of barytes in an aqueous solution of arsenic acid; or, according to Berzelius, by dropping barytes water

<sup>\*</sup> Rose, Ann. de Chim. et de Phys. xxxv. 212.

<sup>†</sup> Ibid. p. 220.

<sup>‡</sup> Dulong, Ann. de Chim. et Phys. ii. 142.

into arsenic acid, till the precipitate becomes permanent. Its properties have not been examined; but it contains water of crystallization, and Mitcherlich has shown, that it is a com-

pound of 2 atoms arsenic acid, and 1 atom barytes.

22. Subsesquarseniate of barytes. This salt was formed by Berzelius by digesting arseniate of barytes in liquid ammonia. It is a white powder, scarcely soluble in water, but slightly soluble, according to Berzelius, in liquid ammonia. This salt was first examined by Laugier. Its constituents, according to the analyses of Laugier and Berzelius, which nearly agree, are

1 atom arsenic acid		•	7.25
1 atom barytes	•	•	14.25
			21.5

23. Diarseniate of barytes. When solutions of chloride of barium and arseniate of ammonia are mixed, this salt is deposited in white, silky, tasteless scales. It is insoluble in water, and composed, according to my analysis, of

l atom arsenic ac	cid	•	7 25
2 atoms barytes	•	•	19
$2\frac{1}{2}$ atoms water	•	•	2.8125
_			
			00.060#

29.0625

24. Terborate of barytes. When a solution of borax is mixed with a liquid barytes salt, a precipitate falls, which, after being well washed, is fused into a transparent glass. It is a transparent grey glass, which reacts as an alkali. Its constituents, as determined by Thenard, Berzelius, and Gmelin, are nearly,

Boracic acid	•	44.2	•	45.1
Barytes .	•	<b>55·8</b>	•	<b>54·9</b>
		100	_	100
ches sufficient	tly near		•	

This approa

3 atoms boracic acid. . l atom barytes . . . 9.5

to leave little doubt about the constitution of the salt.

25. Quaterborate of barytes. Berzelius obtained this salt by mixing chloride of barium with his terborate of ammonia. He found the precipitate to be a compound of

•	Boracic acid Barytes	•	•	•	58·07 41·93
Now this	COM IN THE PORT OF	.] 4	•		100
NOW LINS	comes very near $4\frac{1}{a}$ atoms bora				13.5
	1 atom bary			•	9.5
	_	•			23*

But the accuracy of these analyses of the borates cannot be depended on.

- 26. Silicate of barytes. One part of silica, heated with  $\frac{1}{2}$  part of barytes, melts into a porous porcelain like slag. The same fusion takes place when 2 or 3 parts of barytes are employed. But when the quantity of barytes is 4 times that of the silica, (or nearly an atom of each,) the mixture only melts at the edges, and is opaque.\*
- 27. Selenite of barytes is a white powder insoluble in water, and not altered by exposure to the heat at which glass melts. It is soluble in the strong mineral acids.
- 28. Biselenite of barytes is obtained by dissolving carbonate of barytes in selenic acid till all effervescence is at an end. It crystallizes in round transparent grains. It is soluble in water.
- 29. Antimoniate of barytes. This salt may be formed by mixing antimoniate of potash with muriate of barytes. It is a light flocculent white powder quite insoluble in water. It is not altered by exposure to the air; but nitric acid when boiled with it slowly extracts all the barytes.
- 30. Antimonite of barytes. When antimonite of potash is added drop by drop to a boiling solution of muriate of barytes, the antimonite of barytes crystallizes gradually on the side of the vessel, in the form of small white needles of a silky brilliancy. This salt is slightly soluble in water, and is not altered by exposure to the air.‡
- 31. Tellurate of barytes. A white powder, obtained by dropping tellurate of potash into a solution of chloride of barium.
- 32. Chromate of barytes. Obtained by dropping chloride of barium into bichromate of potash. It has a pale yellow colour,

<sup>\*</sup> Kirwan's Mineralogy, p. 56.

<sup>†</sup> Berzelius, Nicholson's Jour. xxxv. 46.

and is destitute at once of beauty and intensity. It is tasteless sect. v. and anhydrous, and composed of

1 atom chromic acid . . 6.5 1 atom barytes . . . 9.5

16

33. Molybdate of barytes. It may be obtained by dropping acetate of barytes into a solution of molybdate of potash. White flocks fall, which are soon changed into a crystalline powder. When heated to redness it becomes blue, according to Berzelius. It dissolves easily in muriatic or nitric acid, and by spontaneous evaporation is deposited in a saline crust. It is insoluble in water, and seems to contain no water of crystallization, but to be a compound of

1 atom molybdic acid . 9
1 atom barytes . . . 9.5

34. Tungstate of barytes. A white insoluble powder.\*

35. Columbate of barytes. When hydrated columbic acid is digested in chloride of barium with a little ammonia, it is converted into a white powder, composed, according to Berzelius's analysis, of

Columbic acid . 10 or 23.75 Barytes . 4 or 9.5

14

It is therefore a compound of 1 atom of columbic acid, and 1 atom of barytes.

36. Uraniate of barytes. When a mixture of peroxide of uranium, dissolved in muriatic acid and chloride of barium, is precipitated at the boiling temperature by ammonia, and the precipitate is immediately washed on the filter with boiling water, it constitutes a mixture of uraniate of barytes and uraniate of ammonia, which cannot be separated. We obtain uraniate of barytes in a purer state when we drop barytes water into yellow nitrate of uranium. It is a yellowish red powder, composed, according to Berzelius, of

Probably it is a compound of

<sup>\*</sup> Scheele's Memoires, ii. 90.

28	•	•	ium	of urai	peroxide	1 atom		
9.5	•	•	•	•	barytes	1 atom		
					•			
37.5								

- 37. Manganate of barytes. When to manganic acid barytes is added, so as to saturate the acid without occasioning any precipitate, the solution is transparent and violet coloured. It is neutral, but cannot be concentrated or crystallized without decomposition.\*
- 38. Dimanganate of barytes. This salt was obtained by Chevillot and Edwards, by heating to redness equal parts of barytes and deutoxide of manganese; and by Frommherz, by exposing to a red heat a mixture of 2 parts of nitrate of barytes, and 1 part of deutoxide of manganese. It is a light green insoluble powder.†
- 39. Oxalate of barytes. When oxalic acid is dropped into barytes water, a white powder precipitates, which is oxalate of barytes. It is insipid and insoluble in water. It may be obtained equally by mixing solutions of nitrate or muriate of barytes with oxalate of ammonia. Its constituents seem to be

1 atom oxalic acid	•	•	4.5
1 atom barytes		•	9.5
3 atoms water	•	•	3.375
_			
			17.375

I obtained only 3.34 water instead of 3.375.

40. Binoxalate of barytes. When the preceding salt is digested with a solution of oxalic acid, containing just as much acid as exists in the salt, we obtain binoxalate of barytes crystallized in small needles. The same crystals make their appearance when oxalic acid is dropped into concentrated muriate or nitrate of barytes; but if these solutions are largely diluted with water, no precipitate appears. When the binoxalate of barytes is boiled in water, the excess of acid is removed, and the salt falls down in the state of a white powder.‡ The constituents of this salt, according to my analysis, are

2 atoms oxalic acid	•		9
1 atom barytes	• •	•	<b>5</b> ·5
3 atoms water	•	•	3.375

21.875

<sup>\*</sup> Frommherz, Schweigger's Jour. xli. 291. † Ibid. † Bergman, i. 263. See also Fourcroy and Vauquelin, Mem. de l'Instit. ii. 60. and Darracq, Ann. de Chim. xl. 69.

41. Acetate of barytes. This salt may be formed by dissolving barytes or its carbonate in acetic acid, or by decom-

posing the sulphuret of barytes by that acid. By spontaneous evaporation the acetate crystallizes in fine transparent prismatic needles. The primary form of the crystal is a right oblique angled prism. I have obtained it crystallized, as in the figure in the margin, in long flat needles, terminated by a four-sided pyramid. M is inclined to T at an angle of 112° 45′ by my measurement. Mr. Brooke found it 113° 12′. T on c I found 108° 42′. In Mr. Brooke's figure the prism terminated in a bihedral summit, and its acute edges are replaced by tangent planes.\*

Taste saline and bitter; it is soluble in

water, and does not deliquesce when exposed to the air, but rather effloresces. It is decomposed by the fixed alkalies,† by the alkaline carbonates, and by almost all the sulphates. Hence it is often employed to detect the presence of sulphuric acid in solutions. From the experiments of Bucholz, it appears, that 100 of water at the temperature of 60° dissolve about 88 of this salt, and 96 parts when boiling hot. Pure alcohol dissolves  $\frac{1}{100}$  part of its weight while cold, and heat scarcely increases the solvent power of this liquid.‡ Its constituents are as follows:

1 atom acetic acid	•	•	6.25
1 atom barytes	•	•	9.5
3 atoms water	•	•	3.375

19.125

- 42. Lactate of barytes, a gummy matter, which does not crystallize, is easily soluble in water, and does not deliquesce in the air.§
- 43. Formate of barytes. It crystallizes in right oblique four-sided prisms, with angles of 75° 30′, according to the measurement of Bernhardi. The acute edges of the prism are often replaced by tangent planes, and the extremity of the prism terminates in a bihedral summit. The taste of the salt is bitter, and, according to Richter, it effloresces when
  - \* Annals of Philosophy (2d series), vii. 365.
  - † D'Arcet, Ann. de Chim. lxi. 247. † Beitrage, iii. 102.
  - § Braconnot.

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kept in a dry and warm atmosphere; but Gehlen denies this, and I believe with reason. It is soluble in four parts of cold water; but insoluble in alcohol. According to the experiments of Richter, Gehlen, and Göbel, it contains no water of crystallization; but is composed of

1 atom formic acid . 4.625 1 atom barytes . 9.5

14.125

44. Mellate of barytes. When mellitic acid is dropped into acetate of barytes, a flaky precipitate appears, which is dissolved by adding more acid. With muriate of barytes it produces no precipitate; but in a short time a group of transparent needle-form crystals is deposited, consisting most likely of bimellate of barytes.

45. Tartrate of barytes. When concentrated solutions of tartrate of potash, and nitrate of barytes, are mixed, a precipitate of tartrate of barytes falls in small granular crystals. They are nearly tasteless, but leave a slight saline impression in the mouth. Water dissolves a very small proportion of these crystals, and acquires the same taste. When heated they lose no weight, unless the temperature be raised high enough to decompose the acid. Its constituents are

1 atom tartaric acid . 8.25 1 atom barytes . . 9.5

17.75

46. Bitartrate of barytes. Obtained by digesting the preceding salt in tartaric acid. The bitartrate is deposited when the solution is set aside in right prisms with square bases. Taste acid, and reddens vegetable blues. At the temperature of 65°, 100 parts of water dissolve 1.24 of this salt. Its constituents are

_	2	atoms tartaric acid			•	16.5	
š	1	atom barytes				9.5	
		atoms water		•	•	2.25	
			•	•			
						98.95	

- 47. Vinate of barytes, a white insoluble powder.
- 48. Bivinate of barytes. The preceding salt dissolves in tartaric acid, and furnishes small crystals of bivinate.
- 49. Pyrotartrate of barytes. According to Rose, when pyrotartrate of potash is dropt into a solution of nitrate of

barytes, pyrotartrate of barytes precipitates after an interval of some hours.

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- 50. Citrate of barytes. When barytes is added to a solution of citric acid, a flaky precipitate appears, which is at first dissolved again by agitation; but remains permanent when the saturation is complete. The citrate of barytes, thus formed, is precipitated in the state of a white powder; but it gradually assumes the appearance of silky flakes, or forms a kind of vegetation very brilliant and beautiful. It requires a great quantity of water to dissolve it.
- 51. Bicitrate of barytes. This salt may be formed by adding citric acid to barytes water, till the precipitate at first thrown down is again dissolved.
- 52. Pyrocitrate of barytes. When pyrocitric acid is saturated with barytes water, and the solution set aside in a cool place, a white crystalline powder gradually precipitates, which is pyrocitrate of barytes. It is soluble in 150 times its weight of cold water, and in 50 times its weight of boiling water. Its constituents, according to the analysis of Lassaigne, are

Pyrocitric acid . 43.9 or 7.43 Barytes . . 56.1 or 9.5

## 100\*

- 53. Malate of barytes. A gummy uncrystallizable mass, which dissolves in water.+
- 54. Bimalate of barytes. It may be obtained by digesting the preceding salt in malic acid. It is deposited in small crystals; but little soluble in cold water; but easily soluble in boiling water.
- 55. Dimalate of barytes. When a little malic acid is dropt into barytes water, white flocks precipitate, which constitute this salt.
- 56. Pyromalate of barytes. When pyromalic acid is poured into barytes water, white flocks precipitate, but are again dissolved on adding a little cold water. After some hours, the pyromalate of barytes attaches itself to the sides of the glass vessel in small silver white scales. Its constituents, according to Lassaigne, are

<sup>\*</sup> Ann. de Chim. et de Phys. xxi. 105.

<sup>‡</sup> Braconnot.

<sup>†</sup> Braconnot.

<sup>§</sup> Ibid.

100.00\*

- 57. Fungate of barytes. A saltish not crystallizable matter, converted by heat into carbonate of barytes.
- 58. Mucate of barytes. A white powder insoluble in cold, but slightly soluble in boiling water.
- 59. Pyromucate of barytes. Small crystals, not altered by exposure to the air, rather more soluble in hot than in cold water, and insoluble in alcohol.
- 60. Succinate of barytes. This salt, according to Bergman, is difficultly soluble in water. It may be obtained by dropping succinate of ammonia into muriate of barytes. It partly precipitates, and is partly deposited in small crystals on the sides of the vessel.
- 61. Benzoate of barytes. This salt crystallizes, is soluble in hot water, not altered by exposure to the air, but decomposed by heat and by the stronger acids. Its taste is bitter and sharp.
- 62. Gallate of barytes. It is said, that when gallic acid is mixed with barytes water, and air excluded, white flocks of gallate of barytes are thrown down.
- 63. Kinate of barytes. This salt is formed when a solution of kinate of lime in alcohol is mixed with a solution of chloride of barium in weak alcohol. The precipitate being dissolved in weak alcohol, furnishes, when concentrated sufficiently, regular octahedrons. When these crystals are exposed to the air, they become opaque.§
- 64. Meconate of barytes. According to Serturner, this salt is scarcely soluble in water. But Robiquet affirms, that this little solubility is owing to foreign matter with which the salt is usually mixed.
- 65. Boletate of barytes. This salt contains an excess of acid, crystallizes in white plates, and is but little soluble in water, or even in nitric acid. When thrown on a plate of red hot iron it burns with a red flame and remarkable scintillation, leaving carbonate of barytes.
  - 66. Camphorate of barytes. This salt may be obtained by

+ Braconnot.

<sup>\*</sup> Ann. de Chim. et de Phys. xi. 93.

<sup>‡</sup> Houton Labillardiere.

<sup>§</sup> Henry and Plisson, Ann. de Chim. et de Phys. xli. 329.

Braconnot, Ann. de Chim. lxxx. 279.

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boiling carbonate of barytes in an excess of camphoric acid. When the solution is sufficiently concentrated, the camphorate is deposited in white plates. By spontaneous evaporation it may be obtained in small prismatic crystals. It has a saline, bitterish, and hot taste. At the temperature of 59°, 100 parts of water dissolves 55.8 parts of this salt. Its constituents, as determined by M. Rudolph Brandes, are

1 atom camphoric acid

1 atom barytes . . . 9.5

 $3\frac{1}{\alpha}$  atoms water . . . 3.9375

13.4375\*

67. Suberate of barytes. This salt may be formed by boiling carbonate of barytes in a solution of suberic acid. When the liquid is concentrated the suberate falls down, partly in plates, and partly in powder. It is destitute of taste and smell. When heated, it melts, and is destroyed by a sufficiently high temperature, leaving carbonate of barytes. 100 parts of boiling water dissolve 6 parts of this salt, and it is much less soluble in cold water. From Brandes' trials it appears, that at 59°, 100 parts of water dissolve only 1·3 parts of the salt. It seems to contain no water of crystallization.† 68. Stearate of barytes. To form this salt, heat barytes

68. Stearate of barytes. To form this salt, heat barytes water to the boiling temperature, and filter it while hot into a matrass with a long neck, containing stearic acid and boiling water. Boil for two hours, then stop up the mouth of the matrass, and when cold decant off the barytes water, and wash the stearate with boiling water. Finally, digest it with alcohol, to remove the excess of stearic acid. The stearate thus formed is a white, insipid powder, which melts when heated.‡

69. Margarate of barytes. It may be prepared by the same process, and is similar in its properties, to stearate of barytes.§

70. Phocenate of barytes. To obtain this salt, neutralize barytes water with phocenic acid, and allow the solution to evaporate spontaneously. The phocenate crystallizes. The crystals are large transparent octahedrons, easily reduced to powder. It has no smell when pure; but when kept moist it is partially decomposed, and the phocenic acid disengaged conveys a smell to the surrounding atmosphere. Its taste is

<sup>\*</sup> Schweigger's Jour. xxxviii. 293.

<sup>+</sup> Brandes, Schweigger's Jour. xxxiii. 38.

<sup>†</sup> Chevreul, sur les corps gras, p. 53.

hot, sharp, alkaline, sweetish. It reacts slightly as an alkali on reddened litmus paper. At 68° water dissolves its own weight of this salt. It is not sensibly deliquescent.\*

71. Butyrate of barytes. When barytes water is saturated with butyric acid, and the solution sufficiently concentrated, butyrate of barytes crystallizes in long flat prisms. It has a strong smell of fresh butter. Its taste is alkaline and hot, with the flavour of butter. At the temperature of 50°, 100 parts of water dissolve 36.07 of this salt. Alcohol dissolves it, but the salt appears to suffer a partial decomposition.

72. Oleate of barytes. This salt may be formed by boiling barytes water with oleic acid, in the same way as stearate of barytes. It is white, insipid, and destitute of smell, insoluble

in water, but slightly soluble in boiling alcohol.

When digested in oleic acid it is dissolved. When the proper proportions are employed, a binoleate is formed, which

dissolves in alcohol, and reddens litmus paper.

- 73. Caproate of barytes. This salt may be prepared in the same way as the butyrate. It crystallizes in hexagonal plates. While moist, they are very brilliant; but when exposed to the air, they effloresce, and assume the appearance of talc. At 50°, 100 parts of water dissolve 8.02 of this salt. When the solution is kept in a temperature of 86°, the salt crystallizes in needles. It acquires the smell of caproic acid when kept moist, and exposed to the air, obviously from decomposition.
- 74. Caprate of barytes. It may be formed by neutralizing barytes water by hydrated capric acid. It crystallizes in brilliant scales, having a fatty lustre. Its taste is weak and alkaline, and bitter, with something of the flavour of capric acid. At 68°, 100 parts of water dissolve half a part of this salt. When the solution is left to itself, the salt undergoes spontaneous decomposition. When distilled, it leaves a residue of carbonate of barytes, while some carbonic acid and carburetted hydrogen are evolved, and a yellow liquid distilled over.
- 75. Cholesterate of barytes. A red powder, destitute of taste and smell, and very little soluble in water.
- 76. Pinate of barytes. Resembles in appearance precipitated barytes; but when digested in boiling water, it concretes into a porous, resinous looking mass. It is insoluble in alco-

<sup>\*</sup> Chevreul, sur les corps gras, p. 105. † Ibid. p. 120. † Ibid. p. 138. | Ibid. p. 146.

<sup>¶</sup> Pelletier and Caventou, Ann. de Chim. et de Phys. vi. 401.

hol, and scarcely soluble in an alcoholic solution of pinic acid; but it dissolves readily in ether.\*

77. Silvate of barytes. This salt may be obtained by double decomposition, by mixing solutions of silvate of ammonia and of a barytes salt. It dissolves in 5000 times its weight of water, in 6 times its weight of absolute alcohol, and it is still more soluble in that liquid when boiling hot. On cooling, it precipitates in white flocks, which are soluble in ether.

- 78. Carbazotate of barytes. It may be obtained by mixing carbonate of barytes and carbazotic acid with a quantity of water. It crystallizes in four-sided prisms, having a dark colour, and is difficultly soluble in water. When heated it melts, and is decomposed with a very loud explosion, with a yellowish and very brilliant flame. This explosion is not inferior to that produced by fulminate of silver. From the analysis of Liebeg, it seems when crystallized to be a compound of 1 atom anhydrous carbazotate of barytes and 8 atoms water.‡
- 79. Indigotate of barytes. When we form this salt by saturating indigotic acid with carbonate of barytes, we do not obtain it neutral, there is always a portion of di-indigotate formed at the same time. When ammonia is poured into a solution of this salt a yellow powder precipitates, very little soluble in water, whether cold or hot. When heated, it burns with a slight detonation, and, according to the analysis of Buff, is composed of

1 atom indigotic acid,  $2\frac{1}{\sigma}$  atoms barytes.§

- 80. Urate of barytes. A white powder scarcely distinguishable from uric acid.
- 81. Pyrurate of barytes. A white powder very little soluble in cold water.
- 82. Aspartate of barytes. A friable mass composed of small white opaque crystals, having the taste of an aspartate without bitterness.
- 83. Allentoate of barytes. It forms small prismatic white needles. It has an acrid taste, is soluble in water, and is readily decomposed by sulphuric acid.\*\*

84. Sulphovinate of barytes. Vogel formed this salt by

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<sup>\*</sup> Unverdorben, Poggendorf's Annalen, xi. 232. † Ibid. p. 399.

<sup>‡</sup> Liebig, Ann. de Chim. et de Phys. xxxv. 83.

<sup>§</sup> Ann. de Chim. et de Phys. xli. 177.

<sup>||</sup> Chevallier and Lassaigne, ibid. xiii. 160.

<sup>¶</sup> Plisson, ibid. xl. 313. \*\* Lassaigne, ibid. xvii. 302.

saturating the residue remaining after the preparation of sulphuric ether with barytes. The filtered solution set aside (after being concentrated) in a flat porcelain dish, gradually deposited crystals of sulphovinate of barytes. The crystals are transparent prisms, not altered by exposure to the air. They are very soluble in water, but very slightly so in absolute alcohol.\*

85. Sulphonaphthalate of barytes. Mr. Faraday obtained two neutral sulphonaphthalates of barytes, which he distinguished by the names of flaming and glowing salts, from the mode in which they burn. They are formed by rubbing carbonate of barytes with sulphonaphthalic acid, and dissolving the salt in water. The flaming salt, obtained by slow evaporation, forms tufts, which are imperfectly crystalline. deposited rapidly from a hot solution it forms a soft granular When dry, it is white and soft, and is not altered by exposure to the air. It has a bitter taste, is readily soluble in water and alcohol, but insoluble in ether. When heated on platinum foil it burns with a bright smoky flame like naphthaline. When heated above 500° naphthaline may be separated from it. When burned, it leaves a mixture of charcoal, sulphuret of barium, and sulphate of barytes. It is not altered by nitric acid, nitromuriatic acid, nor chlorine.

The glowing sulphonaphthalate was obtained after the undissolved portion (from digesting carbonate of barytes and sulphonapthalic acid) had been repeatedly washed with water. After the fifth washing the salt dissolved is chiefly the glowing kind. It is obtained by evaporation in small crystalline groups. The crystals are prismatic, colourless, and transparent. They are almost tasteless, and much less soluble in water than the other salt. The solution in alcohol is neutral. When heated on platinum foil it burns like tinder, leaving a carbonaceous mixture of sulphuret and sulphate.+

- 86. Vegetosulphate of barytes. A gummy like matter, very soluble in water.
- 87. Sinapate of barytes forms sometimes small needles which effloresce in the air, sometimes a mamillated mass. It is very soluble in water.

<sup>\*</sup> Vogel, Gilbert's Annalen, lxiii. 91.

<sup>†</sup> Faraday, Annals of Philosophy (2d series), xii. 208.

<sup>‡</sup> Braconnot, Ann. de Chim. et de Phys. xii. 186.

<sup>§</sup> Henry and Garot.

## SECTION VI. - SALTS OF STRONTIAN.

- 1. The salts of strontian are in general more soluble than characters, the salts of barytes, but less so than the salts of lime.
- 2. The greater number of them are capable of assuming a crystallized form, though they are not more given to crystallize than the salts of barytes.
- 3. Solutions of strontian are precipitated by the sulphates, phosphates, and oxalates.
- 4. We can distinguish a salt of strontian from a salt of barytes by means of succinate of ammonia. When we drop this salt into a solution of a salt of strontian no precipitate falls; but a precipitate immediately appears if we drop it into a salt of barytes.
- 5. When a piece of paper dipped into a solution of a salt of strontian is set on fire, it burns with a red flame. But if it be dipped into a salt of barytes, or of lime, it burns with a yellow flame.
- 6. When a current of fluosilicic acid gas is passed through a solution of strontian in muriatic acid no precipitate falls; but when the same gas is passed through a solution of barytes a precipitate immediately falls.
- 7. Salts of strontian are not precipitated by prussiate of potash.
- 8. Salts of strontian are not poisonous, as is the case with salts of barytes.
- 1. Sulphate of strontian. This mineral exists in considerable quantities, most commonly in the new red sandstone formation. Sometimes in amorphous masses, but more commonly foliated or crystallized.

The primary form of the crystal is a right rhombic prism, the faces of which meet at angles of 104° and 76°. This is the same figure as sulphate of barytes, from which it differs by about 2° 20′ of greater obliquity. It affects the same modifications as sulphate of barytes. Tasteless, translucent, or almost transparent. Lustre vitreous. Specific gravity about 3.86. Colour when pure, white; but it has usually a blue tint, on which account it has received the name of coelestine. It is said to fuse in a high heat into a glass. Not sensibly soluble in cold water. It is said to be soluble in 3840 times its weight of boiling water. It dissolves in concentrated sulphuric acid, and is precipitated when the acid is diluted with water, as was first observed by Dr. Hope. Its constituents are

	sulphuric strontian	acid	•	•	5 6·5
					11.5

2. Sulphite of strontian. A white tasteless powder, scarcely soluble in water, and when exposed to the air gradually changed into sulphate. It is anhydrous, and composed of

1 atom sulphurous acid . 4
1 atom strontian . 6.5

10.5

3. Hyposulphite of strontian. When a solution of sulphuret of strontian is exposed to the air for a few days it becomes colourless, some sulphur and carbonate of strontian being deposited. When this deposite is removed by the filter, the clear liquid yields by evaporation fine transparent rhomboidal crystals somewhat flattened. These crystals are not altered by exposure to the air at the temperature of 77°, but at 122° they effloresce like sulphate of lime when calcined. They still continue unaltered, excepting the loss of their water of crystallization. At the temperature of 50° water dissolves the sixth part of its weight of this salt.\*

Mr. Herschell formed this salt by passing a current of sulphurous acid through sulphohydrate of strontian. Its taste is purely bitter. It dissolves in about  $1\frac{3}{4}$  times its weight of hot water. It is insoluble in alcohol. It dissolves chloride of silver with great facility. When heated, it becomes white, without losing its figure, and burns with a very faint flame. Its constituents, according to the analysis of Gay-Lussac, are

2 atoms hyposulphurous acid
1 atom strontian . . . 6.5
5 atoms water . . . 5:625

4. Hyposulphate of strontian. This salt may be formed in the same way as hyposulphate of barytes. The crystals are dodecahedrons, composed of two six-sided pyramids applied base to base; the face of one pyramid is inclined to the corresponding face of the other at an angle of about 120°, and the apices of the pyramids are truncated very deep, so as to convert the crystal into a six-sided table with bevelled edges. This salt dissolves in 1.5 times its weight of boiling water, and

<sup>\*</sup> Gay-Lussac, Ann. de Chim. lxxxv. 199. † Edin. Philos. Jour. i. 20.

in 4.5 times its weight of water at 60°. It has a bitter taste, sect. VI. is not altered by exposure to the air, and when heated decrepitates feebly. According to the analysis of Heeren, it is composed of

1 atom hyposulphuric acid . 9
1 atom strontian . . 6.5
4 atoms water . . . 4.5
20\*

5. Anhydrous nitrate of strontian. This salt was first formed by Dr. Hope; it was afterwards examined by Klaproth and Pelletier; but the most complete description of it was published by Vauquelin about the end of the year 1797.† It may be prepared either by dissolving carbonate of strontian in nitric acid, or by decomposing sulphuret of strontian by means of that acid. The solution is to be evaporated to dryness, redissolved in water, and evaporated slowly till the salt crystallizes.

Nitrate of strontian crystallizes in regular octahedrons or cubo-octahedrons. It is perfectly transparent. Its lustre is adamantine. It has a strong pungent cooling taste. Its specific gravity is 3.006. It is soluble in its own weight of water at the temperature of 60°, and in little more than half its weight of boiling water. It is insoluble in alcohol. It is not altered by exposure to the air. It deflagrates on hot coals. Subjected to heat in a crucible, it decrepitates gently, and then melts. In a red heat it boils, and the acid is dissipated. If a combustible substance be at this time brought into contact with it, a deflagration with a very vivid red flame is produced.‡ It is by means of this decomposition that strontian is obtained in the greatest purity. When a crystal of nitrate of strontian is put into the wick of a candle, it communicates a beautiful purple flame.

Its constituents are as follows:

1 atom nitric acid		•	6·7 <b>5</b>
1 atom strontian	•	•	6.2

13.25

6. Hydrous nitrate of strontian. When an aqueous solution of nitrate of strontian, sufficiently concentrated, is set aside for crystallization, crystals of hydrated nitrate of strontian are sometimes deposited. These crystals are transparent, have a

II.

<sup>\*</sup> Heeren, Poggendorf's Annalen, vii. 177.

<sup>†</sup> Jour. de Min. An. vi. 7. ‡ Hope, Edin. Trans. iv. 12.

vitreous lustre, and speedily effloresce when exposed to the

air. The cas represent measurement P on M or The edges or even to respectively two new respectively.

air. The crystals are oblique rhombic prisms, as represented in the margin. The following measurements were made by Mr. Brooke. P on M or M' 103° 40'; M on M' 66° 20'. The edges g are sometimes replaced by one, or even two planes, inclined to M and M' respectively at angles of 150° 10'. These two new planes are inclined to each other at

an angle of 126°.\*

When this hydrous salt is heated it melts in its water of crystallization. Its constituents are

1 atom nitric ac	eid	•	•	6.75
1 atom strontian	nù	•	•	6.5
4 atoms water	•	•	•	4.5
		-		17.75

7. Chlorate of strontian. This salt was prepared and purified by Mr. Chenevix by the same processes as the chloride of strontian, with which indeed it agrees in most of its properties. It is deliquescent, and more soluble in alcohol than chloride of of strontian. It crystallizes in needles, which melt in the mouth, and produce the sensation of cold. On burning coals it fuses rapidly, producing a beautiful purple flame. Its constituents, according to the analysis of Chenevix, would seem to be

1 atom chloric acid	•	•	9.5
1 atom strontian	•	•	6.2
5 atoms water	•	•	5.625

21.625+

8. Iodate of strontian. This salt is obtained in the same way as the preceding. It forms small crystals, which, when viewed by the microscope, appear to be octahedrons. One hundred parts of boiling water dissolve 0.73 of this salt; 100 parts of water at 59° dissolve only 0.24 of it. It contains water of crystallization. When exposed to heat it exhibits exactly the same phenomena as iodate of barytes.‡ Its constituents are

1 atom iodic acid	•	•	20.75
1 atom strontian	•	•	6.5
			27.25

<sup>\*</sup> Annals of Philosophy (2d series), vii. 288. † Phil. Trans. 1802.

<sup>‡</sup> Gay-Lussac, Ann. de Chim. xci. 84.

9. Carbonate of strontian. This salt exists native, but so far as Sect. VI. I know, not in a state of purity. It is easily formed by pouring an alkaline carbonate into a solution of nitrate of strontian. A white, tasteless, insoluble powder, falls, which is carbonate of strontian. According to Dr. Hope, it requires, 1536 parts of boiling water to dissolve it.\* Its specific gravity is about 3.66. It is not altered by exposure to the air. When strongly heated in a crucible, it loses part of its acid, and this decomposition is facilitated by making it into a paste with charcoal powder. According to Saussure, it melts into a transparent glass at the temperature of 226° Wedgewood.+ When thrown in powder on burning coals, it produces red sparks. It is anhydrous, and is composed of

1	atom	carbonic a	acid	•	•	2.75
1	atom	strontian			•	6.5
						9.25

When dried in the open air it retains about 8 per cent. of water. This, which amounts to about \$\frac{4}{2}ths of an atom, is probably merely hygrometrical water.

At Strontian, in Argyleshire, there are two varieties of carbonate of strontian, one of which has a light green colour, and the other is brown. The green is a compound of 10 atoms carbonate of strontian, and 1 atom carbonate of lime, while the brown is a compound of 8 atoms carbonate of strontian and 1 atom carbonate of lime.

The carbonate of strontian is slightly soluble in water impregnated with carbonic acid. No doubt the solution consists of bicarbonate; but this salt can only be obtained dissolved in water.

10. Phosphate of strontian. A white, tasteless, insoluble powder, which fuses before the blow-pipe into a white enamel. Its constituents, no doubt, are

1 atom phosphoric a	acid	•	4.5
I atom strontian	•	•	6.5
	•		11

It would appear from the analysis of this salt by Stromeyer, that it sometimes contains an excess of strontian amounting to 1th of an atom.

- 11. When the last species is dissolved in phosphoric acid a biphosphate of strontian is formed, which has not hitherto been particularly examined.
  - \* Hope, Trans. Edin. iv. 5. † Jour. de Phys. xlv. 24.

- 12. Phosphite of strontian. This salt may be obtained by mixing chloride of strontian with a watery solution of chloride of phosphorus. It is slightly soluble in water, and crystallizes when the solution is exposed to spontaneous evaporation. When heated, phosphate of strontian is formed, while phosphuretted hydrogen gas is driven off.\*
- 13. Hypophosphite of strontian. A very soluble salt, which crystallizes with difficulty.
- 14. Arseniate of strontian. When solutions of nitrate of strontian and arseniate of soda in atomic proportions are mixed together, no immediate precipitate falls; but when the solution is set aside for 24 hours arseniate of strontian is deposited in small crystals on the sides of the vessel. These crystals are very minute rectangular four-sided prisms, destitute of taste, and not acting on vegetable blues. 100 parts of water at 60° dissolve 0.284 of this salt. Its constituents, by my analysis, are

l atom arsenic acid	•	•	7.25
1 atom strontian	•	•	6.5
8 atoms water	•	•	9.0

22.75

- 15. The arseniate dissolves in arsenic acid, and doubtless forms a binarseniate which has not been examined.
- 16. Borate of strontian. This salt has only been formed by Dr. Hope. It is a white powder, soluble in about 130 parts of boiling water. The solution turns the syrup of violets green.‡
- 17. Silicate of strontian. When silica is heated with thrice its weight of strontian, a gray coloured cohering mass is obtained, almost destitute of taste, very little soluble in water, but readily dissolving in aqueous solutions of the acids, which do not form insoluble salts with strontian.§
- 18. Selenite of strontian. The neutral selenite is a white insoluble powder. Biselenite is obtained by dissolving carbonate of strontian in selenious acid. When slowly evaporated, the salt is deposited in the state of a white crust, very difficultly soluble in water, even at a boiling temperature. When heated, it melts, gives out its water of crystallization, swells, and forms a porous mass, from which the heat gradually separates the

<sup>\*</sup> Dulong; Mitcherlich, Ann. de Chim. et de Phys. xxxv. 213.

<sup>†</sup> Dulong, Ann. de Chim. et Phys. ii. 142.

<sup>‡</sup> Hope, Edin. Trans. iv. 17. § Vauquelin.

excess of acid. The neutral selenite does not liquefy when sect. VI.

19. Chromate of strontian. This salt is precipitated when solutions of chromate of potash and nitrate of strontian are mixed together. It is a fine yellow powder, tasteless, and insoluble in water and alcohol; but it dissolves in nitric and muriatic acids. When exposed to a red heat it loses no weight; hence it is anhydrous, and composed of

1 atom chromic acid	•	•	6.5
l atom strontian	•	•	6.5
			13

20. Molybdate of strontian. An insoluble powder.

- 21. Manganate of strontian. Neither Chevillot and Edwards, nor Frommherz were able to form this salt. When 1 part of black oxide of manganese, and two parts of nitrate of strontian are heated together in a crucible, a light green matter is obtained, insoluble in water, which is probably dimanganate of strontian. When strontian water is added slowly to manganesic acid, the red colour gradually disappears, and a light green matter obtained, probably of the same nature.†
- 22. Oxalate of strontian. This salt, first examined by Dr. Hope and afterwards by Vauquelin, may be readily formed by mixing together a solution of oxalate of potash and nitrate of strontian. The oxalate of strontian immediately precipitates. It is a white insipid powder; soluble in 1920 parts of boiling water. Its constituents, by my analysis, are

1 atom oxalic acid		•	4.5
1 atom strontian	•	•	6.5
2 atoms water	•	•	2.25
			13.25

23. Binoxalate of strontian. This salt may be formed by digesting the preceding in a solution of oxalic acid in water. It crystallizes in pretty large four-sided prisms, feels harsh, reddens vegetable blues, and is very sparingly soluble in water. Its constituents, by my analysis, are

2 atoms oxalic acid	•	•	9
1 atom strontian	•	•	6.5
			15.5

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 263.

<sup>†</sup> Frommherz, Schweigger's Jour. xli. 292.

ined by Dr. Hope, and afterwards by Vauquelin, is easily formed by dissolving strontian or its carbonate in acetic acid. It crystallizes in pretty long four-sided prisms, with bases appearing to the eye rectangular. But from Mr. Brooke's measurements, it appears that the primary form is a right oblique angled prism, whose faces are inclined to each other at angles of 96° 10′, and 83° 50′.\* The taste of this salt is sharp, which gives it an impression of bitterness. It has a silky lustre, and is pretty soluble in water. It undergoes no alteration when exposed to the atmosphere. Its constituents, by my analysis, are

1 atom acetic acid	•	•	•	6.25
1 atom strontian	•	•	•	6.5
l atom water		•	•	1.125
				13.875

25. Lactate of strontian. Lactic acid dissolves carbonate of strontian disengaging the carbonic acid. The solution when concentrated by evaporation assumes the form of mucilage; but in 24 hours it becomes solid, has a whitish colour, is semitransparent, and consists of a congeries of globular bodies resembling the form which malate of lime assumes. At the temperature of about 70°, this salt is soluble in eight times its weight of water.†

26. Formate of strontian. This salt crystallizes in transparent six-sided prisms. When heated it becomes first opaque, and then falls into a white powder. Its constituents are

1 atom formic acid	•	•	4.62
1 atom strontian		•	6.5
4 atoms water	•	•	2.5

13.625‡

27. Mellate of strontian. A white powder insoluble in water, but soluble in muriatic acid.§

28. Tartrate of strontian. This salt, first examined by Dr. Hope, and afterwards by Vauquelin, may be formed by dissolving strontian in tartaric acid, or by mixing together solutions of nitrate of strontian and tartrate of potash. When these

<sup>\*</sup> Annals of Philosophy (2d series), vii. 288.

<sup>+</sup> Braconnot, Ann. de Chim. lxxxvi. 87.

<sup>‡</sup> Göbel, Schweigger's Jour. xxxii. 348.

<sup>§</sup> Klaproth, Beitrage, iii. 114.

two solutions are mixed in the atomic proportions, no precipitate appears at first, but on setting the mixture aside, tartrate of strontian is gradually deposited in oblique rhomboids, with angles of 113° 20′ and 66° 40′. This salt is tasteless, and insoluble in water. Its constituents, by my analysis, are

1 atom tartaric acid	•		8.25
1 atom strontian	•		6.5
3 atoms water	•	•	3.375
			19.105
•			18.125

- 29. Vinate of strontian. When vinate of soda and nitrate of strontian are mixed, vinate of strontian is deposited in white bulky flocks, insoluble in water, and scarcely soluble in an excess of vinic acid.
- 30. Citrate of strontian. This salt was obtained by Vauquelin by mixing a solution of citrate of ammonia with nitrate of strontian. No precipitate appears; but when the liquid is slowly evaporated, small crystals of citrate of strontian are gradually formed. This salt is soluble in water, and exhibits nearly the same properties as the oxalate or tartrate of strontian.\*
- 31. Malate of strontian. Obtained by saturating malic acid with strontian water. When rapidly evaporated it assumes the form of a gummy mass; but by slow evaporation it may be obtained in white translucent crystalline grains. It is very soluble in water.+
- 32. Bimalate of strontian. It precipitates when the neutral solution is mixed with malic acid. It is in small crystals; little soluble in cold water; but easily soluble in boiling water.+
- 33. Mucate of strontian. Strontian water throws down from mucate of potash, white tasteless flocks, insoluble in cold, but soluble in hot water. They dissolve also in mucic acid.
- 34. Pyromucate of strontian. Small crystals not altered by exposure to the air, and rather more soluble in hot than in cold water.
- 35. Succinate of strontian. This salt may be formed by saturating strontian water with succinic acid. When the solution is evaporated the succinate of strontian precipitates in small crystals as fine as sand. The taste of this salt has some resemblance to that of muriate of potash. It is equally soluble in hot and in cold water. When a little of it is dropped into barytes water, succinate of barytes immediately precipitates.§

<sup>\*</sup> Jour. de Min. An. vi. p. 16. + Braconnot.

<sup>‡</sup> Labillardiere. § Moretti, Ann. de Chim. lxxxvi. 270.

- 36. Benzoate of strontian. This salt crystallizes. The crystals when exposed to the air lose their lustre; but do not effloresce. They are scarcely soluble in cold, but dissolve readily in hot water.
  - 37. Gallate of strontian. Like gallate of barytes.
- 38. Camphorate of strontian. It may be prepared by dissolving carbonate of strontian in camphoric acid. It crystallizes in translucent and white plates, and is not more soluble in water than camphorate of barytes. Its taste is saline and bitter. When heated it behaves like camphorate of barytes.\*
- 39. Suberate of strontian. This salt may be prepared by boiling carbonate of strontian in a solution of suberic acid. This salt is deposited in translucent crusts, destitute of any regular form. Its taste is saline and bitterish. Its solubility in water is as follows:

At 122°	100	water	dissolves	7.5	salt
86	100			6.4	
68	100			4.6	
212	100			8.7	

Its constituents, as determined by Brandes, from whom the preceding facts have been obtained, are as follows:

Suberic acid	•	•	65.48
Strontian	•	•	34.52

100.+

- 40. Stearate of strontian. It is prepared in the same way as stearate of barytes, and its properties are similar.‡
- 41. Margarate of strontian. Also similar both in its preparation and properties to margarate of barytes.
  - 42. Oleate of strontian. Also similar to oleate of barytes.
- 43. Phocenate of strontian. It may be obtained by neutralizing strontian water with phocenic acid. When evaporated in vacuo over quicklime, it yields long prismatic crystals which effloresce when exposed to the air. Its smell is that of phocenic acid. Its taste similar to that of phocenate of barytes. It is very soluble in water. When heated it melts, and at the same time undergoes decomposition.
- 44. Butyrate of strontian. Similar in its properties to butyrate of barytes. Water at 39° dissolves the third part of its weight of this salt.\*\*

<sup>\*</sup> Brandes, Schweigger's Jour. xxxviii. 295.

<sup>†</sup> Chevreul, sur les corps gras, p. 55.

<sup>#</sup> Ibid. p. 92. ¶ Ibid. p. 108.

<sup>†</sup> Ibid. xxxiii. 90.

<sup>§</sup> Ibid. p. 68. \*\* Ibid. p. 123.

- 45. Caproate of strontian. It crystallizes in plates, transparent while in the liquid; but assuming the appearance of enamel when exposed to the air. At 50° 100 water dissolve 9.05 of this salt.\*
- 46. Caprate of strontian. Obtained by saturating strontian water with capric acid, and leaving the solution exposed to the air. At the temperature of 64° 100 parts of water dissolve half a part of this salt.+
- 47. Cholesterate of strontian. An orange-yellow powder, almost insoluble in water.
- 48. Urate of strontian. A white insoluble powder, scarcely distinguishable in appearance from uric acid.
- 49. Sulphonaphthalate of strontian. This salt very much resembles the flaming sulphonaphthalate of barytes. It is white but not distinctly crystallized. It is soluble in water and alcohol, not altered by exposure to the air, and when heated burns with a bright flame, without any red tinge.§
- 50. Sinapate of strontian. Similar to sinapate of barytes; but has less tendency to crystallize.

## SECTION VII. - SALTS OF LIME.

- 1. A considerable number of the salts of lime are insoluble characters, in water. Some of those which are soluble cannot easily be crystallized.
- 2. When a salt of lime is insoluble in water, if we boil it for some time in a solution of carbonate of potash, a white powder remains, which is soluble with effervescence in nitric acid, and which possesses all the characters of carbonate of lime.
- 3. The soluble salts of lime are not altered by the addition of pure ammonia, but the addition of potash or soda occasions a white precipitate to fall, which is pure lime.
- 4. When oxalate of ammonia is dropped into a salt of lime, a dense white precipitate immediately begins to make its appearance; but citrate or tartrate of ammonia does not occasion an immediate precipitation.
- 5. The salts of lime are not precipitated by prussiate of potash; but some of them are precipitated when the infusion of nutgalls is mixed with them.
- 1. Hydrated sulphate of lime. This salt was well known to the ancients under the name of gypsum; but the composition of

§ Faraday, Annals of Philosophy (2d series), xii. 209.

<sup>\*</sup> Chevreul, sur les corps gras, p. 139. † Ibid. p. 149.

<sup>‡</sup> Pelletier and Caventou; Ann. de Chim. et de Phys. vi. 401.

gypsum was not known till Margraff\* and Lavoisier† analyzed it, and proved it to be a compound of sulphuric acid and lime. The salt formed by the artificial union of these two bodies was formerly called *selenite*, probably from its whiteness.

The properties of this salt were first examined with precision by Bergman. It is found abundantly in different parts of the world, particularly in the new red sandstone formation, in which it often accompanies common salt. It occurs granular, foliated, and fibrous, and frequently also crystallized. primary crystal is a right oblique prism, whose faces are inclined to each other at angles of 113° 8' and 66° 52'. most common shape is a thin rhomboidal prism, with bevelled edges. Sometimes perfectly transparent and colourless. Lustre silky, very soft. Specific gravity 2.322.1 It has a slightly nauseous taste, scarcely perceptible, except by drinking a glass of water impregnated with it.§ It is soluble in 460 parts of water at the temperature of 60, | and in 450 of boiling water. Mr. Paul has observed, that if this solution be saturated by pressure with hydrogen gas, the sulphate in about six months is converted into a sulphuret. The salt is not affected by exposure to the air. It is soluble in sulphuric acid.

When heated, it loses its water of crystallization, decrepitates, and falls into a soft white powder. This powder, when its water has been driven off by the application of a red heat, absorbs water very rapidly, and solidifies it; at the same time a slight increase of temperature takes place: so that if it be formed into a paste with water, it dries in a few minutes. In this state, but mixed with a portion of carbonate of lime, it is called *Plaster of Paris*, and is much employed for forming casts, &c. in consequence of this property.

Sulphate of lime, when exposed to a violent heat, melts; before the blow-pipe it gives an opaque vitreous globule. The temperature necessary to produce this effect is, according to Saussure, 51° of Wedgewood.\*\* Its constituents are as follows:

1 atom sulphuric	acid	•	•	5
1 atom lime	•	•	•	3.5
2 atoms water	•	•	•	2.25
				10.75

<sup>\*</sup> Mem. Berlin, 1750, p. 144. † Mem. Paris, 1768, p. 341.

<sup>‡</sup> Roget and Dumas; Annals of Philosophy (2d series), iii. 392.

<sup>§</sup> Macquer. || Bucholz, Gehlen's Journal, v. 165.

<sup>¶</sup> Phil. Mag. xv. 63. \*\* Jour. de Phys. xlv. 16.

2. Anhydrous sulphate of lime. This species is found native sect. VII. in different parts of the world, usually accompanying or interspersed through the preceding species. It is said also occasionally to accompany metallic ores. It seems to have been first pointed out by Haiiy. A specimen of it was described with much precision by Fleurieu in the Journal de Physique for 1798; and analyzed by Vauquelin, who first ascertained its composition. It has since been described with more accuracy by Bournon,\* and a purer specimen of it analyzed by Chenevix, + and by Klaproth. ±

It is often amorphous, but frequently also crystallized. The primary form of the crystals is a right rectangular prism, the lateral edges of which are frequently replaced by tangent planes. Its specific gravity is about 2.960. Its hardness is considerable, being not inferior to that of calcareous spar. It usually phosphoresces when heated. It is transparent, insoluble in water, and in its other properties agrees with common sulphate. Its constituents are

1 atom sulphuric acid	•	•	5
1 atom lime .	•	•	3.5
			8.5

Sometimes it is found converted into the hydrous sulphate by absorbing moisture. In such cases it is easily distinguished by its cleavage from the species to which it has been converted. It is usually denominated anhydrite by mineralogists.

2. Sulphite of lime. This salt was first mentioned by Berthollet, and described by Fourcroy and Vauquelin.

When obtained by saturating carbonate of lime by sulphurous acid, it has the form of a white powder; but if an excess of sulphurous acid be added, it dissolves, and crystallizes on cooling in six-sided prisms, terminated by long six-sided pyramids. It has scarcely any taste; however, when kept long in the mouth, it communicates to the tongue a taste which is manifestly sulphureous. It requires about 800 parts of water to dissolve it. When exposed to the air it effloresces very slowly, and its surface is changed into sulphate of lime. When heated, it loses its water of crystallization, and falls to powder. A violent heat disengages some sulphur, and converts it into sulphate of lime.

<sup>\*</sup> Jour. de Min. An. x. ii. 355.

<sup>†</sup> Ibid. p. 418.

I am not aware of any analysis of it by a modern chemist.

Probably the constituents are

1 atom sulphurous a	acid	•	•	4
l atom lime	•	•	•	3.5
2 atoms water	•	•	•	2.25
				0.55

It dissolves in sulphurous acid, and probably forms a bisulphite, which has not been examined.

3. Hyposulphite of lime. When a solution of sulphuret of lime is exposed to the air it loses its colour in a few days, and some sulphur and carbonate of lime precipitate, which are easily removed by the filter. When the liquid is evaporated, it yields crystals in prisms somewhat similar to the crystals of muriate of lime. These crystals may be preserved in the open air without undergoing any alteration. They are soluble in water, and consist of hyposulphite of lime.\*

Mr. Herschell has found that this salt may be obtained in considerable quantity by passing a current of sulphurous acid through the liquid formed by boiling a mixture of flowers of sulphur and quicklime in a sufficient quantity of water. When the liquid is evaporated at a temperature not exceeding 130°, it yields on cooling large and beautiful crystals most commonly in the shape of irregular six-sided pirsms, which refract doubly. Water, at the temperature of 37°, dissolves nearly its own weight of this salt, and the temperature falls to 31°. The specific gravity of a solution saturated at 50° is 1.300, and when the specific gravity is 1.114371 at 60°, the solution contains 0.2081 of its weight of the salt. These crystals are not altered by exposure to the air. They are insoluble in alcohol of the specific gravity 0.82344. From the analysis of Herschell, the salt seems a compound of

1 atom hyposulpl	hurous :	acid	•	•	5
1 atom lime .	•	•	•	•	3.5
6 atoms water	•	•	•	•	6.75

15.25+

4. Hyposulphate of lime. This salt is easily formed by precipitating hyposulphate of manganese by lime, filtering and concentrating the solution. The salt crystallizes, and the

<sup>\*</sup> Gay-Lussac, Ann. de Chim. lxxxv. 200.

<sup>†</sup> Edin. Phil. Jour. i. 14.

shape of the crystals is very nearly the same as that of hypo-sulphate of strontian. The taste is pure bitter. The crystals are not altered by exposure to the air. One part of the crystals dissolve in 0.8 part of boiling water, and in 2.46 parts of water at the temperature of 66°. Alcohol does not dissolve it; but appears to deprive it of a portion of its water of crystallization. Its constituents are

1 atom hyposulphuric acid 1 atom lime . 4 atoms water 17.0\*

5. Nitrate of lime. This salt has been long known to chemists. Native nitre is almost always contaminated with it. It may be prepared by dissolving carbonate of lime in nitric acid; evaporating the solution to the consistence of a syrup, and then allowing it to cool slowly. The salt is precipitated in the state of crystals.

Its crystals are six-sided prisms, terminated by long pyramids; but it is oftener obtained in the form of long slender brilliant needles. Its taste is very acrid and bitter. Its specific gravity is 1.6207.† Scarcely any salt is more soluble in water. At the temperature of 60°, one part of water dissolves four parts of nitrate of lime, and boiling water dissolves any quantity of it whatever. Boiling alcohol dissolves its own weight of it. † Considerable difficulty attends its crystallization, as is the case with all very soluble salts. When exposed to the air, it very soon attracts moisture, and melts altogether. This strong affinity for moisture renders it sometimes useful for drying the gases. They are made to pass through tubes containing dried nitrate of lime; and this salt, during their passage through it, abstracts great part of the water which they hold in solution.

This nitrate, when heated, readily undergoes the watery fusion. When the water of crystallization is evaporated, the salt becomes dry, and often acquires the property of shining in the dark. In that state it was formerly known by the name of Balduin's phosphorus; because this property of nitrate of lime was first pointed out by Balduin. When strongly heated

<sup>\*</sup> Heeren, Poggendorf's Annalen, vii. 178.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 12. ‡ Bergman, i. 136. § His account of it was published in 1675, under the title of Phosphorus Hermeticus, seu Magnes Luminaris. See also Phil. Trans. Ab. ii. 368.

it is decomposed; nitrous gas, oxygen gas, and azotic gas are emitted, and the pure lime remains behind. This salt scarcely possesses the property of detonating with combustible bodies, in consequence probably of the greater proportion of its water of crystallization.

Its constituents, according to my analysis, are

l atom nitric acid	•	•	6.75
1 atom lime .	•	•	3.5
3 atoms water	•	•	3· <b>3</b> 75
•			

13.625

When a solution of this salt is concentrated in the vacuum of an air-pump over sulphuric acid, it becomes a thick syrup, which on the least agitation concretes into a white solid mass, with the evolution of a good deal of heat. This mass I found composed of

1 atom nitric acid	•	•	6.75
1 atom lime .	•	•	3.5
6 atoms water	•	•	6.75
			<del></del>
			3

17

6. Chlorate of lime. This salt may be procured and purified in the same way as the chlorate of barytes. It is very deliquescent, and undergoes the watery fusion when slightly heated. Alcohol dissolves it copiously. Its taste is sharp and bitter; and when it dissolves in the mouth, it produces a strong sensation of cold. From Chenevix's analysis, it is probable that its constituents are

1 atom chloric ac	cid .	٠	9.5
1 atom lime			3.5
2 atoms water .		•	2.25
			<del></del>

15.25

The water obtained exceeded a little two atoms, being 2.57 instead of 2.25.

7. Iodate of lime. This salt may be obtained by dissolving carbonate of lime in iodic acid, or by mixing a salt with base of lime and iodate of potash. It is usually in powder; but it may be obtained in crystals, by dissolving it in the solution of muriate or hydriodate of lime. Its crystals are small quadrangular prisms. One hundred parts of boiling water dissolve 0.98 of this salt; 100 parts of water at the temperature of 64½° dissolve 0.22 of it. The phenomena which take place

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when it is exposed to heat are similar to those which appear when iodate of potash is heated, excepting only that iodate of lime requires a stronger heat to decompose it. Its water of crystallization amounts to about 3 per cent.\* The constituents of this salt are

8. Carbonate of lime. This substance, under the names of marble, chalk, limestone, &c. exists in great abundance in nature, variously mixed with other bodies. It is perhaps the most important and most generally used of all the salts, unless we except common salt. Its properties of course have been very completely investigated.

It is often found crystallized and perfectly transparent. The primitive form of its crystals is the obtuse rhomboid with angles of  $105^{\circ}$  5', as determined by Dr. Wollaston. But, besides the primitive, no less than 616 varieties of its crystals have been discovered and described by mineralogists. It has scarcely any taste. Its specific gravity is 2.717. It is insoluble in pure water; but water saturated with carbonic acid dissolves  $\frac{1}{1300}$ th part of it; from this solution it gradually precipitates, as the acid leaves it, in the form of a white powder.† It suffers little or no alteration by being exposed to the air. When exposed to heat, it decrepitates, and afterwards its acid separates as the heat is increased: but to separate the acid completely, a pretty strong heat is required.

Its constituents are

1 atom carbo	nic acid	•	2.75
1 atom lime		•	3.5
			6.25

Some very interesting experiments on the fusibility of this salt were made by Sir James Hall. The result was, that when the carbonic acid is prevented from making its escape by strong compression, the salt melts at a red heat, and assumes an appearance which has some resemblance to granular limestone. A portion of the carbonic acid is usually dissipated. This portion is sometimes very small, and very often it does not exceed 4 or 5 per cent. Bucholz has verified these expe-

<sup>\*</sup> Gay-Lussac, Ann. de Chim. xci. 84.

riments in a very unexpected manner. He put  $4\frac{1}{2}$  pounds of washed chalk (carbonate of lime with only 0.005 of foreign matter) into a crucible, pressed it strongly down, and exposed it covered to a strong heat in a furnace. The chalk, except a small portion on the surface, was converted into a foliated, hard, yellowish mass, having considerable transparency, which evidently had undergone a commencement of fusion. It was obviously in a similar state with Sir James Hall's carbonate of lime, and contained 42 per cent. of carbonic acid.\* Here the same effect was produced without compression. It must have depended, no doubt, upon the degree of heat to which the crucible was exposed.

- 9. Bicarbonate of lime. When a current of carbonic acid gas is passed through water in which carbonate of lime in powder is suspended, a solution is effected. When a calcareous solution is precipitated by an alkaline bicarbonate, the more the liquid is dilute, the more of the lime remains in solution. It is obvious from these facts, that lime is capable of combining with two atoms of carbonic acid, and that the bicarbonate is soluble in water. It is in this way that lime is frequently held in solution in mineral waters. But bicarbonate of lime can only be formed in water, when we attempt to separate the salt, and to get it in a dry state, the second atom of carbonic acid always separates.
- 10. Phosphate of lime. This salt is obtained when phosphate of soda and chloride of calcium are mixed in atomic proportions. The phosphate of lime precipitates in white flocks. But a small quantity remains in solution, and can only be obtained by evaporating the solution to dryness, and pouring water on the residue.

Phosphate of lime, thus prepared, is always in the state of a white powder. It is destitute of taste, insoluble in water, and not liable to be altered by exposure to the air. It may be exposed to a strong heat without undergoing any change; but in a very violent heat it becomes soft, and is converted into a white semitransparent enamel, or rather porcelain. According to the experiments of Saussure, a heat of 378° Wedgewood is necessary to produce this effect.† It is soluble in nitric and muriatic acid without effervescence, and may be again precipitated from them unaltered by muriate of ammonia.

<sup>\*</sup> Gehlen's Jour. 2d series, i. 271.

Sulphuric, nitric, muriatic, fluoric, and several vegetable Sect. VII. acids are capable of decomposing phosphate of lime; but the decomposition is only partial.

Its constituents are

1 atom phosp	•	4.5		
1 atom lime	•	•	•	3.5
		•		-
				8

11. Sesquiphosphate of lime. This salt was first obtained by Berzelius. He formed it by mixing a solution of phosphate of lime in phosphoric acid with alcohol. It is a white matter, which reddens litmus paper. Water removes the excess of acid, and leaves the neutral phosphate. Its constituents are

11/2	atom	phosp	horic	acid	•	6.75
1	atom	lime	•	•	•	3.5
						10.05

The proportion of water has not been determined.

- 12. Biphosphate of lime. If we digest phosphate of lime in pure phosphoric acid dissolved in hot water, the acid will be found to take up a quantity of phosphate containing exactly its own weight of phosphoric acid; but it refuses to dissolve any more. I consider, therefore, this solution as a biphosphate of lime. It has an acid and rather disagreeable harsh taste. When slowly evaporated to dryness, it does not crystallize, but forms a dry white mass, somewhat deliquescent in the air and soluble in water, but not in acids. Before the blow-pipe it melts into a transparent tasteless glass, insoluble in water, and incapable of acting on vegetable blues. No acid dissolves it.
- 13. Quaterphosphate of lime. If phosphate of lime in fine powder be digested for some time with as much sulphuric acid as is capable of saturating the whole of the lime which it contains; if it be then diluted with a sufficient quantity of water and thrown upon a filter, the liquid which passes through contains the whole of the phosphoric acid \* still combined with one-fourth of the lime which originally existed in the salt. The other three-fourths have been abstracted by the sulphuric acid, and remain upon the filter. This liquid, therefore, contains, in solution, a quaterphosphate of lime. This is the salt

II.

<sup>\*</sup> About a third of the phosphate of lime is not decomposed, but I abstract this quantity.

described by Fourcroy and Vauquelin, in 1795, under the name of superphosphate of lime. When evaporated, it forms soft crusts, which have an acid taste, and are soluble in water. When heated, it readily melts before the blow-pipe into a transparent tasteless glass, insoluble in water and acids, and not affecting vegetable blues. This is the well-known substance from which phosphoric acid is made. It is sold by apothecaries under the name of glassy phosphoric acid. If it be mixed with a quantity of bicarbonate of potash and exposed to a red heat, it is decomposed and converted into phosphate of potash and common phosphate of lime. By this treatment 22 grains of common phosphate of lime may be obtained from 50 grains of the glassy salt.

14. Subsesquiphosphate of lime. This is the mineral which occurs native, and is known to mineralogists by the name of apatite or asparagus stone. It is usually crystallized in low six-sided prisms. Its colour varies, but is most commonly white or green. It has a great deal of lustre, which is resinous. Its fracture is imperfectly foliated. It is soft, and its specific gravity varies from 2.824 to 3.2. It is clear from the analysis of Klaproth, that it is a compound of

1	atom	phosp	hori	c acid	•	4.5
$1\frac{1}{2}$	atom	lime		•	•	3.75

8.25

It is obvious from Berthier's experiments, that this salt is formed when phosphate of ammonia is mixed with an excess of chloride of calcium.\*

Besides these five species of phosphates, there are probably some others, but they have not been hitherto described.

15. Phosphite of lime. A white powder, slightly soluble in water. When heated, it is converted into phosphate, giving out only traces of water, and a gas which burns with a blue flame (obviously hydrogen). Its constituents are

1 atom phosphorous acid				•	3.5	
1 atom	lime	•		•	•	3.5
1 atom	water		•	•	•	1.125

8.125

<sup>16.</sup> Hypophosphite of lime. This salt is very soluble in water; but its properties have not been particularly examined.

Sect. VII.

17. Arseniate of lime. This salt exists native, and is known to mineralogists by the name of pharmacolite. It is often amorphous, but sometimes in small hair-like crystals. It may be formed artificially by mixing a solution of arsenic acid with lime-water, taking care not to saturate the acid completely. It is a tasteless white powder, insoluble in water, but soluble in nitric or muriatic acid. It dissolves also, according to Pfaff, in sulphate, nitrate, and muriate of ammonia. Its constituents are

 1 atom arsenic acid
 .
 7.25

 1 atom lime
 .
 .

 3 atoms water
 .
 .

14.125\*

- 18. Sub-sesquarseniate of lime. This salt was formed by Mitcherlich by mixing solutions of chloride of calcium and arseniate of potash, soda, and ammonia. The solution becomes sour, and the subsesquarseniate precipitates.
- 19. Binarseniate of lime. Arseniate of lime dissolves in arsenic acid, and the solution, when sufficiently concentrated, deposites small crystals of binarseniate of lime.
- 20. Borate of lime. This salt may be formed by mixing together lime-water and the aqueous solution of boracic acid, or by boiling together lime and pure borax in water. In either case, the borate of lime precipitates in the state of a white powder, tasteless, and difficultly soluble in water.+
- 21. Silicate of lime. No simple silicate of lime has hitherto been met with in the mineral kingdom. But there occur no fewer than three species composed of silica and lime; namely,
  - (1.) Sesquisilicate of lime.
  - (2.) Bisilicate of lime, or table spar.
- (3.) Tersilicate of lime. A white mineral, which has been found near Christiania, and has been considered as a variety of tremolite, but which, in fact, is a compound of three atoms silicic acid and one atom lime.
- 22. Selenite of lime. It is very imperfectly soluble in water. It precipitates by degrees when we dissolve carbonate of lime in selenic acid. It constitutes, when dry, a soft powder very similar to carbonate of lime. When heated to redness it melts, and if the fusion takes place in a glass vessel it corrodes the glass and gradually passes through it.
  - 23. Biselenite of lime is obtained by dissolving the selenite

in selenious acid. It crystallizes in small prisms which are not altered by exposure to the air. Ammonia deprives it of the half of its acid. Heat produces the same effect.\*

24. Antimoniate of lime. This salt may be obtained by pouring a solution of antimoniate of potash into muriate of lime. It is a white powder, sparingly soluble in water. The precipitate assumes a crystalline form, precisely like that of carbonate of lime.+

25. Antimonite of lime. A white crystalline powder, very little soluble in water.

26. Tellurate of lime. A white powder formed by dropping tellurate of potash into a solution of chloride of calcium.§

27. Chromate of lime. A fine yellow powder, tasteless, and insoluble in water, easily formed by double decomposition. Its constituents are

1 atom chromic	acid	•	•	6.5
1 atom lime	•	•	•	3.5
				10

28. Molybdate of lime. Formed by pouring a solution of molybdate of potash into chloride of calcium. It is a white powder, insoluble in water.

29. Tungstate of lime. This salt occurs native, crystallized in octahedrons composed of two four-sided pyramids with a square base. It was first analyzed by Scheele under the name tungsten (heavystone). It is of a yellowish-gray colour, and sometimes crystallized, and always somewhat transparent. Its specific gravity is about 6, and its hardness is generally considerable. It is insoluble in water, and is not sensibly altered by exposure to heat. According to the analysis of Berzelius, || it is composed of

1 atom	tunstic	acid	•	•	15.5
1 atom	lime	•	•	•	3.5
			•		
					10

30. Columbate of lime. An insoluble white powder.

31. Uranjate of lime. When pernitrate of uranium and chloride of calcium are mixed, and the solution precipitated by ammonia, the yellow precipitate which falls is a compound of oxide of uranium and lime, as was first observed by Bucholz.

† Berzelius, Nicholson's Jour. xxxv. 41. ‡ Ibid. 45.

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 263.

<sup>§</sup> Ibid. xxxvi. 131. Af handlingar, iv. 305.

32. Manganate of lime. The salts of lime occasion no precipitate when dropped into manganate of potash.\* From this it would appear that manganate of lime is soluble in water.

33. Oxalate of lime. This salt is readily formed by mixing solutions of oxalate of ammonia and chloride of calcium. The oxalate of lime immediately precipitates in the state of a white insipid powder, insoluble in water, and communicating a green colour to the syrup of violets. This salt is in the form of a white powder, tasteless, and perfectly insoluble in water. But it dissolves in almost all acids with considerable facility; of course, it is not precipitated from liquids if they contain an excess of acid. Its constituents, when simply dried by exposure to the air, are

1 atom oxalic a	cid	•	•	4.5
1 atom lime	•	•	•	<b>3·5</b>
2 atoms water	•	•	•	2.25

10.25

A heat of 500° is required to render this salt anhydrous.

Oxalate of lime may be decomposed by sulphuric acid, and likewise by digestion with a solution of carbonate of potash. Laugier announced that it was decomposed also when digested with caustic potash.† Probably his alkali had been partly in the state of carbonate.

I have tried unsuccessfully to form a binoxalate of lime.

34. Croconate of lime. When a mixture of solutions of croconate of potash and chloride of calcium is set aside for some time croconate of lime is deposited in small lemon-yellow crystalline grains, which are soluble in water, to which they communicate a yellow colour.

35. Acetate of lime. This salt was first described accurately by Crollius. The ancients, however, used a mixture of lime and vinegar in surgery.§ It is easily formed by dissolving chalk in acetic acid. When the solution is evaporated till a pellicle forms on its surface, it yields, on cooling, the acetate of lime in fine prismatic needles of a glossy appearance like satin. Its specific gravity is 1.005.

Its taste is bitter and sour, because it has an excess of acid. It is soluble in water. It is not altered by exposure to the air,

<sup>\*</sup> Frommherz, Schweigger's Jour. xli. 280.

<sup>†</sup> Ann. de Chim. et de Phys. xxvi. 217.

<sup>‡</sup> L. Gmelin.

<sup>§</sup> Plinii, lib. xxxvi. c. 24.

<sup>||</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

at least Morveau kept some of it for a whole year merely covered with paper, and even quite uncovered for a month, without its undergoing any alteration.\* Heat decomposes it by disengaging, and, at the same time, partly decomposing its acid. Mr. Mills has observed that when the dry salt is heated to 250° and then rubbed with a stiff spatula, it becomes highly luminous.† The constituents of this salt, by my analysis, are

l'atom acetic a	cid		•	6.25
1 atom lime	•	•	•	3.5
6 atoms water	•			6.75
				٠

16.5

- 36. Binacetate of lime. When the preceding salt is dissolved in acetic acid, and the solution concentrated, it deposites crystals of binacetate of lime.
- 37. Lactate of lime. A gummy mass, which, when digested in alcohol, is divided into two portions. 1. A pure lactate of lime is dissolved, and gives a shining varnish inclining to a light yellow colour, which, when slowly dried, cracks all over and becomes opaque. 2. The insoluble portion is a submalate. It is a powder which, by exposure to the air, becomes smooth like gum, or like malate of lime.‡ The lactate when sufficiently concentrated forms confused crystals which resemble cauliflower. It is very white, opaque, has little taste, and as it were efflorescing. It dissolves in 21 times its weight of cold water. When heated, it melts into a transparent liquid, then swells, blackens, takes fire, and leaves carbonate of lime.§
- 38. Formate of lime. This salt crystallizes in six-sided prisms, terminated by six-sided pyramids, || and likewise in octahedrons. Its taste is saline and bitterish. It effloresces in the air. Decrepitates when heated. At the temperature 64° it dissolves in ten times its weight of water. It is insoluble in alcohol.
- 39. Mellate of lime. When mellate of ammonia is mixed with chloride of calcium bulky flocks fall, which gradually assume the form of white light needles, having a silky lustre. When dried, they retain about 0.21 of water.\*\* Hence the constituents of this salt are
  - \* Morveau, Encycl. Method. i. 9.
  - † Annals of Philosophy (2d series), vii. 235.
  - # Berzelius, Djurkemien, ii. 437.
  - § Braconnot, Ann. de Chim. lxxxvi. 87.
  - || Suersen. | ¶ Göbel.
  - \*\* Wöhler, Poggendorf's Annalen, vii. 330.

Sect. VII.

 1 atom mellitic acid
 .
 6.5

 1 atom lime
 .
 .
 3.5

 2 atoms water
 .
 .
 2.25

10.25\*

40. Tartrate of lime. This salt may be formed by dissolving lime in tartaric acid, or more economically by dissolving tartar in boiling water, and adding to the solution carbonate of lime in powder till it ceases to produce any effervescence, and to redden vegetable blues. Tartrate of lime precipitates in the state of a white powder, tasteless, nearly insoluble in cold water, but soluble in 600 parts of boiling water. It is fre-

quently found in crude tartar crystallized in octahedrons composed of two four-sided pyramids applied base to base. The common base is a rectangle. The figure in the margin represents this crystal. The measurements are

i on i' . . . 100° y on y' . . . 90

It is rendered soluble in water by an excess of acid, or by being mixed with some of the soluble tartrates, as tartar and Rochelle salt. When in the state of a dry powder, it contains a very considerable portion of water, from which it can scarcely be freed by a long exposure to heat. Its constituents, by my analysis, are

1 atom tartaric	acid	•		8.25
1 atom lime	•	•	•	3.5
4 atoms water	•	•	•	4.5
				16.25

- 41. Vinate of lime. When vinic acid is dropped into lime water white flocks precipitate, consisting, according to Walchner, of exceedingly fine needles. Vinic acid precipitates nitrate and muriate of lime. This salt scarcely dissolves in vinic acid, but it dissolves in muriatic acid, and is again precipitated by ammonia.
- 42. Pyrotartrate of lime. When pyrotartrate of potash is mixed with chloride of calcium, a precipitate gradually falls. This salt is scarcely soluble in water, unless it contain an excess of acid.+
- \* The quantity of water actually found was 2.65, or a surplus of about one-third of an atom.

<sup>+</sup> Rose.

43. Citrate of lime. This salt is formed by dissolving carbonate of lime in citric acid. It is usually in the state of a white powder scarcely soluble in water; but it is soluble in an excess of acid, and may be obtained from that solution in crystals. Its constituents are

1 atom citric acid		. •	7.25
1 atom lime .	•	•	3.5
			<del></del>
			10.75

44. Pyrocitrate of lime. A white mass, composed of cottony needles. The taste is sharp, at 50° it dissolves in 25 times its weight of water. It is composed, according to Lassaigne, of

Pyrocita	ric ac	id	•		46.66
Lime		•		•	<b>2</b> 3·33
Water	•	•	•	•	30.00
					100

If we were to consider the atomic weight of pyrocitric acid to be 7, the constituents would be

I atom pyrocitri	c acid	•	•	7
1 atom lime	•	•	•	3.5
4 atoms water	•	•	•	4.5
•				

45. Malate of lime. When malic acid is neutralized with lime, it forms a salt scarcely soluble in water, which may be obtained in crystals, by allowing the supermalate of lime to evaporate spontaneously. Crystals of neutral malate are formed in the solution.\* But this acid has a strong tendency to combine in excess with lime, and to form a supermalate of lime. This salt is formed when carbonate of lime is thrown into malic acid, or into any liquid containing it. This supersalt exists in various vegetables, especially the sempervivum tectorum, and some of the sedums.

Supermalate of lime has an acid taste. It yields a precipitate with alkalies, sulphuric acid, and oxalic acid. Lime water saturates the excess of acid, and throws down a precipitate of malate of lime. When the supermalate of lime is evaporated to dryness, it assumes exactly the appearance of gum arabic; and if it has been spread thin upon the nail or wood, it forms a varnish. It is not so soluble in water as gum arabic, and the

<sup>\*</sup> Scheele, Crell's Annals, ii. 5. Eng. Trans.

taste readily distinguishes the two. Supermalate of lime is insoluble in alcohol.\* This salt always reddens vegetable blues.

The constituents of the bimalate, as determined by Braconnot, are

2 atoms malic acid	•	•	17.0
1 atom lime .	•	•	3.5
6 atoms water.	•	•	6.75
			27.25

According to this statement, the atomic weight of malic acid is 8.5.

- 46. Dimalate of lime. This salt is formed when malic acid is dropped into an excess of lime water. It precipitates in white flocks.†
- 47. Pyromalate of lime. Pyromalic acid occasions no precipitate in lime water.
- 48. Fungate of lime. Fungate of potash does not precipitate chloride of calcium. But when a solution of lime in fungic acid is concentrated, the salt is deposited in plates, which appear to be oblique, four-sided prisms. Taste saline. Not altered by exposure to the air. It requires about 80 times its weight of cold water to dissolve it.§
- 49. Mucate of lime. A white powder, insoluble in water. But the bimucate is a soluble salt.
- 50. Pyromucate of lime. Small crystals, not altered by exposure to the air. More soluble in hot than cold water, and insoluble in alcohol.
- 51. Succinate of lime. This salt forms oblong, pointed, non-deliquescent crystals, which are difficultly soluble even in boiling water. It is not altered by exposure to the air. It is decomposed by muriate of ammonia, and by the fixed alkaline carbonates.
- 52. Benzoate of lime. This salt forms white, shining, pointed crystals, of a sweetish taste, much more soluble in hot than in cold water. It exists in abundance in the urine of cows. One hundred parts of cold water dissolve 5 parts of this salt. When heated it melts, gives out water and some benzoic acid. When the heat is increased, an empyreumatic acid is separated similar to balsam of Peru.
  - \* Scheele, Vauquelin, Ann. de Chim. xxxv. 54.
  - † Braconnot. ‡ Lassaigne.
  - § Braconnot, Ann. de Chim. lxxxvii. 242.
  - || Fourcroy and Vauquelin.
  - ¶ Bucholz, Gehlen's Journal für die Chemie, Physick, &c. ix. 348.

- Class I. 53. Gallate of lime. Similar to gallate of barytes.
  - This salt may be obtained by mace-54. Kinate of lime. rating yellow Peruvian bark in water, concentrating the liquid, and setting it aside for spontaneous evaporation.

It is white, crystallizes in square or rhomboidal plates, has no taste, and is flexible under the teeth.

It dissolves in about five times its weight of water of the temperature of 55°. It is insoluble in alcohol.

On burning coals, it swells, giving out the smell of tartar, and leaving a mixture of carbonate of lime and charcoal.

The fixed alkalies and their carbonates precipitate lime from the solution of this salt, but ammonia produces no effect. Sulphuric and oxalic acids precipitate lime likewise; but neither acetate of lead nor nitrate of silver produce any effect.

55. Meconate of lime. It crystallizes in prisms, and is but little soluble in water. According to Choulant it is composed of

Meconic	$\mathbf{acid}$		•	•	34
Lime	•	•	•		42
Water	•	•	•	•	24

100

According to this analysis, the atomic weight of meconic acid is only 2.83 (a very unlikely circumstance). Were we to consider it as a compound of

2 atoms oxygen	•	•	2
1 atom carbon			0.75
1 atom hydrogen	•	•	0.125
			2.875

its atomic weight would be 2.875, and meconate of lime would be a compound of

1 atom meconic a	cid	•	2.875
l atom lime .	•	•	3.5
2 atoms water	•	•	2.25
			8.625

- 56. Boletate of lime. Four-sided prisms, having a bitterish taste, decomposed by sulphuric and oxalic acid, and soluble in 110 times their weight of cold water.
- 57. Camphorate of lime. This salt may be formed by boiling carbonate of lime and camphoric acid in a flask with water, filtering the solution, and then neutralizing it with lime water. When sufficiently concentrated, crystals of camphorate of lime

are deposited, the shape of which, according to Bernhardi, is sect. vu. a four-sided oblique prism, the faces of which are inclined to each other at angles of 120° and 60°. The taste is bitterish and astringent. It is soluble, according to Bucholz, in 5 times its weight of cold water, and, according to Brandes, very soluble in hot water. When heated, it becomes opaque, assumes a brown colour without melting, and at last catches fire and burns with flame. According to the analysis of Brandes, its constituents are

> Camphoric acid 47.965 Lime . 14.535 Water 37.500

> > 100.000\*

Probably the true constitution of the salt is as follows:

1 atom camphoric acid 13.375 1 atom lime 3.5 8 atoms water 9.0

25.875

58. Suberate of lime. This salt may be prepared by boiling a mixture of suberic acid and carbonate of lime in water, till all evolution of carbonic acid is at an end. When the filtered liquid is concentrated, the suberate is deposited in powder or in plates. This salt does not crystallize. It is perfectly white: it has a slightly saltish taste: it does not redden the tincture of turnsole. It is very sparingly soluble in water except when hot; and as the solution cools most of the salt precipitates again. When placed upon burning coals it swells up, the acid is decomposed, and there remains only the lime in the state of powder.+ According to the experiments of Brandes, 100 parts of water at the temperature of 59° dissolve 0.25 of this salt.1

- 59. Stearate of lime. This salt may be obtained by mixing solutions of chloride of calcium and stearate of potash. The precipitate must be washed till the water employed neither precipitates nitrate of silver nor oxalate of ammonia. Its properties are similar to those of stearate of barytes. §

  60. Margarate of lime. The properties of this salt are quite
- similar to those of the preceding one.

<sup>\*</sup> Schweigger's Jour. xxxviii. 289.

<sup>†</sup> Ann. de Chim, xxiii. 53.

<sup>1</sup> Schweigger's Jour. xxxiii. 86.

<sup>§</sup> Chevreul, sur les corps gras, p. 58.

<sup>|</sup> Ibid. p. 68.

- 61. Oleate of lime. When hot solutions of chloride of calcium and oleate of potash are mixed, oleate of lime precipitates. It is white and pulverulent when dry. It melts when exposed to a gentle heat.\*
- 62. Phocenate of lime. It may be formed by neutralizing phocenic acid in solution in water by carbonate of lime. When the solution thus obtained is concentrated in vacuo over quicklime, phocenate of lime crystallizes in prisms. It is soluble in water, and possesses characters analogous to those of phocenate of barytes.†
- 63. Butyrate of lime. This salt may be prepared in the same way as butyrate of barytes. It crystallizes in very small prismatic needles, and is transparent. At 60°, 100 parts of water dissolve 17.58 parts of this salt. When this solution is heated, the salt crystallizes so abundantly, that the liquid becomes solid. But it again dissolves when cooled down to 60°.

Two parts of butyrate of lime, and 3 of butyrate of barytes, dissolved in water, and left to spontaneous evaporation, deposite octahedrons, consisting of the two salts in combination.

- 64. Caproate of lime. This salt crystallizes in brilliant plates, many of which are squares.§
- 65. Cholesterate of lime. This salt is very little soluble in water.
- 66. Pinate of lime. It may be formed when a calcareous salt is dropped into a solution of pinate of potash. It falls in the state of a yellowish white powder. It has no resemblance to a resin, and does not become coherent when exposed to the heat of boiling water. It is slightly soluble in alcohol, very soluble in ether, and in oil of turpentine and olive oil. Its constituents, according to Unverdorben, are

105.17||

67. Silvate of lime. It may be prepared by a process similar to that which yields the preceding salt. It dissolves in about 5000 times its weight of water. It is slightly soluble in alcohol of the specific gravity of 0.883; but it dissolves in 6 times its weight of absolute alcohol, and it is still more soluble when the alcohol is boiling hot. As the solution cools,

<sup>\*</sup> Chevreul, sur les corps gras, p. 93. † Ibid. p. 109. † Ibid. p. 124. § Ibid. p. 140. | Poggendorf's Annalen, vii. 314.

the salt is deposited in white flocks, which before the micro- sect. VIL scope appear crystalline. These flocks dissolve in ether. When the ether solutions is mixed with absolute alcohol, and left to spontaneous evaporation, the silvate is deposited in colourless grains, which appear under the microscope as small spherical masses attached to each other.\*

- 68. Carbazotate of lime. Obtained by the same process as carbazotate of barytes. Crystals flat, four-sided prisms, very soluble in water. They detonate like carbazotate of potash.
- 69. Urate of lime. A white powder, scarcely distinguishable in appearance from uric acid.
- 70. Pyrurate of lime. This salt crystallizes in mamillary masses, it is soluble in water, and has a bitter and slightly acrid taste. When gently heated it melts, and on cooling assumes the appearance of yellow wax. When calcined in a platinum crucible, it leaves 8.6 per cent. of pure lime.;
- 71. Aspartate of lime. This salt forms a gummy mass. taste is similar to that of aspartate of soda. When boiled with carbonate of lime it becomes sensibly alkaline.§
- 72. Hydro-carbo-sulphate of lime. This salt is obtained by mixing a solution of chloride of calcium in alcohol, with a solution of hydro-carbo-sulphate of potash, chloride of potassium is precipitated, and hydro-carbo-sulphate of lime remains pretty pure, dissolved in the alcohol. || The properties of this salt have not been investigated.
- 73. Sulphovinate of lime. This salt may be obtained by saturating the residue after the preparation of ether with carbonate of lime, filtering the solution, and setting it aside to spontaneous crystallization. The crystals are long four-sided tables, not altered by exposure to the air. The taste is sweetish. The salt dissolves readily in water and in alcohol. When placed in vacuo over sulphuric acid, the crystals lose their water of crystallization and become opaque. When heated to redness they take fire and burn with flame, leaving sulphate of lime behind. When distilled in a retort it loses its water of crystallization, then becomes black, giving out an empyreumatic ether, with a white heavy oil which sinks in water. At the

<sup>\*</sup> Unverdorben, Poggendorf's Annalen, xi. 399.

<sup>+</sup> Liebig, Ann. de Chim. et de Phys. xxxv. 84.

<sup>†</sup> Chevallier and Lassaigne, ibid. xiii. 160.

<sup>§</sup> Plisson, ibid. xl. 314.

<sup>|</sup> Zeise, Annals of Philosophy (2d series), iv. 244.

same time a quantity of sulphurous acid gas is extricated. There remains in the retort sulphate of lime mixed with charcoal.\*

- 74. Sulphonaphthalate of lime. A white salt with a bitter taste, soluble in alcohol, and when the solution is evaporated imperfect crystals are deposited. It burns with flame.
- 75. Sinapate of lime is very soluble in water, and shoots into mamillary masses.‡

## SECTION VIII. - SALTS OF MAGNESIA.

The salts of magnesia can scarcely be said to have been known till Dr. Black published his celebrated experiments on magnesia alba, and quicklime, in the year 1755. They were afterwards examined more in detail by Bergman, and different salts of magnesia have been since described by different chemists.

Characters.

- 1. A very great proportion of them is soluble in water, and capable of crystallizing.
- 2. When any of the fixed alkalies or of their carbonates is dropped into a salt of magnesia a white flocky precipitate falls.
- 3. No precipitate appears when sulphate of soda is dropped into a salt of magnesia.
- 4. If phosphate of soda be dropped into a salt of magnesia, no precipitate appears; but if any ammonia be added, a white precipitate falls, which is a double salt composed of phosphoric acid, ammonia, and magnesia. This precipitation furnishes the best method yet known for separating magnesia from other bodies, and determining its quantity. It was first pointed out by Dr. Wollaston.
- 5. Prussiate of potash occasions no precipitate in a salt of magnesia, unless the acid happen to have a metal for its basis.
- 6. Magnesia has a greater tendency than any of the bases whose salts have been already described to enter into double compounds. The base with which it is most given to unite is ammonia.
- 7. When a salt of magnesia is tinged with a little nitrate of cobalt, and fused before the blow-pipe with a strong blast, it assumes a fine *flesh* colour, the tint of which is very feeble, and not easily distinguished till the assay is perfectly cold. This fact was discovered by Assessor Gahn, and was used by him with success to discover the presence of magnesia in mineral

<sup>\*</sup> Vogel, Gilbert's Annalen, lxiii. 90.

<sup>†</sup> Faraday, Annals of Philosophy (2d series), xii. 210.

<sup>†</sup> Henry and Garot.

It answers also with several of the salts of magnesia; sect. VIII. but when the acid is combustible or volatile, and leaves pure magnesia, we are not able to accomplish the fusion by the blowpipe, in such cases we must add borax or biphosphate of soda.

1. Sulphate of magnesia. This salt is held in solution in the springs at Epsom in England, and was procured from them by evaporation more than a century ago. Hence the term Epsom salt, by which it was long distinguished. It was called also sal catharticus amarus from its taste and properties, and Seydler salt, because it exists in the Seydler spring at Seydschutch a village in Bohemia. Some account of it was given by Grew in 1675; and in 1723, Mr. Brown published a description of the process employed in extracting it from the springs, and in purifying it.\* In Italy it is manufactured from schistose minerals, containing sulphur and magnesia. By roasting these minerals, and then moistening them and exposing them to the air, the salt effloresces on their surface. By solution in water, with the addition of a little lime to precipitate any metallic substance that may be in solution, and repeated crystallizations, the salt is obtained in a state of purity.+

It exists in considerable quantity in sea-water; and the uncrystallized residuum in the salt pans, after all the common salt has crystallized, consists partly of this salt dissolved in water. This residuum is usually called bittern, and sometimes in Scotland spirit of salt.

Sulphate of magnesia crystallizes in right prisms, the bases of which to the eye appear squares; but from the measurements of Mr. Brooke, it appears that the angles deviate a little from right angles, being 90° 30′ and 89° | 30'. The figure in the margin represents a pretty common form which this salt assumes. The following are the measurements of Mr. Brooke.1

M on M'	•	•	90° 30′
M on h	•	•	134 45
$\mathbf{M}$ on $\boldsymbol{e}$	•	•	129 00
a on $a$	•	•	120 nearly.

The crystals refract double.

<sup>\*</sup> Phil. Trans. xxxii. 348.

<sup>+</sup> Ann. de Chim. xlviii. 80. See also Gehlen's Jour. iii. 549. An account of the manufactory has been published by Dr. Holland in Phil. Trans. 1816, p. 294.

<sup>†</sup> Annals of Philosophy (2d series), vi. 40.

Class L

This salt has an intensely bitter taste. Its specific gravity is 1.66.\* At the temperature of 55° 100 water dissolves 90.01 of the crystals, at 60° it is soluble in its own weight of water, and in less than two-thirds of its weight of boiling water.† The volume of water is increased <sup>4</sup>/<sub>10</sub>ths by adding the salt.‡ When exposed to the air it effloresces, and is reduced to powder. When exposed to heat it undergoes the watery fusion; and by increasing the temperature its water is evaporated, but it cannot be decomposed by means of heat. Before the blow-pipe it melts with difficulty into an opaque vitreous globule.§ Its constituents are

1 atom sulphuric acid	•	•	5
1 atom magnesia	•	•	2.5
7 atoms water	•	•	7.875
			15:375

It appears from the observations of M. Planche, that when dry sulphate of magnesia in powder is mixed with dry bicarbonate of soda, the two powders gradually act upon each other, and a double decomposition takes place.

2. Sulphite of magnesia. This salt has only been examined by Fourcroy and Vauquelin. It is prepared, like the others, by saturating carbonate of magnesia with sulphurous acid; a violent effervescence takes place, and the liquid becomes warm. The sulphite as it forms remains at the bottom in the form of a white powder: but if an excess of acid be added, it dissolves, and may be obtained in crystals by subsequent exposure to the air. Its crystals are white and transparent and in the form of depressed tetrahedrons. Its specific gravity is 1.3802.¶ taste is mild and earthy at first, and afterwards sulphureous. It becomes opaque when exposed to the air; but is very slowly converted into a sulphate. At the temperature of 60° it is soluble in 20 parts of water. Boiling water dissolves a greater proportion of it; but the solution crystallizes on cooling. When its solution in water is exposed to the air, this salt is very soon converted into a sulphate. By exposure to heat, it softens, swells up, and becomes ductile like gum, and loses 0.45 parts of its weight. In a strong heat the acid is disengaged, and

<sup>\*</sup> Hassenfratz, Ann. Chim. xxviii. 12. † Bergman, Opusc. i. 377. ‡ Bergman, Opusc. i. 377. § Ibid.

Annals of Philosophy (2d series), xii. 403.

<sup>¶</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

the earth remains pure. From the analysis of Fourcroy and Sect. VIII.

Vauquelin there is some reason to believe that the constituents of this salt are

1 atom sulphurous	acid	•	. •	4
l atom magnesia	•	•	•	2.5
4 atoms water	•	•	•	4.5
•			•	
				11

- 3. Hyposulphite of magnesia. This salt is easily obtained by boiling a solution of sulphite of magnesia and flowers of sulphur. It has an intensely bitter taste, is very soluble in water, but does not deliquesce when exposed to the air. It readily crystallizes in cooling. When laid on a hot iron it burns with a blue flame, but is incapable of maintaining combustion. Before the flame of the blow-pipe it swells into a fungous mass by the escape of the acid precisely as borax does by that of water. Pure magnesia remains behind.\*
- 4. Hyposulphate of magnesia. This salt may be formed by mixing solutions of sulphate of magnesia and hyposulphate of barytes. The solution may be concentrated by boiling; but hyposulphate of magnesia is so very soluble in water, that it is very difficult to obtain it in regular crystals. The crystals appear to be six-sided prisms, with angles of 120°. When heated they melt in the water of crystallization. At 55° they dissolve in 0.85 of their weight of water. They are not altered by exposure to the air, and have a very bitter taste. From the analysis of Heeren they appear to be composed of

•	1 atom hyposulphuric a	cid	•	•	9
	l atom magnesia	•		•	2.5
	6 atoms water	•	•	•	<b>6.75</b>

8-25+

5. Nitrate of magnesia. The composition of this salt was first ascertained by Dr. Black. Bergman is the only chemist who has given a detailed description of it. It is usually prepared by saturating nitric acid with magnesia, and evaporating to a proper consistency. The salt crystallizes as the solution cools. It crystallizes in rhomboidal prisms, and often in small needles attached to one another. Its taste is very bitter and disagreeable. Its specific gravity is 1.736.‡

<sup>•</sup> Herschell, Edin. Phil. Jour. i. 21.

<sup>+</sup> Poggendorf's Annalen, vii. 179.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

At the temperature of 60° it is soluble in little more than its weight of water, and still more soluble in boiling water. Alcohol of about 0.840 dissolves ½th of its weight of it.\* When exposed to the air it gradually attracts moisture and deliquesces. When heated, it undergoes the watery fusion; and when its water is evaporated, it assumes the form of a dry powder. In a strong heat it gives out a little oxygen gas, then nitrous gas, and lastly nitrous acid; and the earth remains behind in a state of purity.† It scarcely detonates with any of the combustible bodies. Its constituents, by my analysis, are

l atom nitric acid	•	•	6.75
l atom magnesia	•	•	2.5
6 atoms water	•	•	6.75

6. Chlorate of magnesia. This salt may be prepared in the same way as chlorate of lime, which it resembles in most of its properties.

According to the analysis of Mr. Chenevix, its constituents

are

60·0 acid 25·7 magnesia 14·3 water

## 100.0‡

Hence the constituents are probably

1 atom chloric acid	•	•	9.5
l atom magnesia	•	•	2.5
2 atoms water	•	•	2.25
_			

14.25

16.

7. Carbonate of magnesia. This salt occurs native. It is said that even hills of it exist in Hindostan. It may be formed artificially by passing a current of carbonic acid through magnesia dissolved in water, a solution is obtained which deposites small crystals of carbonate of magnesia. It is formed also when solutions of sulphate of magnesia and bicarbonate of potash are mixed. The crystals are oblique rhombic prisms, the faces of which are inclined at angles of 86° 30′ and 93° 30′. The base of the prism makes with the lateral faces an angle of 102°. The acute lateral edges of the prism are often replaced by

<sup>\*</sup> Bergman, i. 136. † Wenzel, p. 85.

<sup>‡</sup> Chenevix on Hyperoxygenized Muriatic Acid. Phil. Trans. 1802.

tangent planes.\* When these crystals are exposed to the air they lose their water and fall to powder. The crystals are tasteless, and dissolve in 48 times their weight of water. They have no sensible taste. Dr. Murray of Belfast has introduced a solution of magnesia in water, acidulated with carbonic acid as a medicine. It seems an excellent preparation where the use of magnesia is indicated.

Native carbonate of magnesia is anhydrous; but the artificial is a compound of

1 atom carbonic acid	•		2.75
l atom magnesia	•	•	2.5
3 atoms water	•	•	3.375

8.625+

The salt which Boussingalt considered as a sesquicarbonate of magnesia is obviously this salt, not quite free from a little hydrated magnesia.

8. Subcarbonate of magnesia. When a hot solution of sulphate of magnesia is precipitated by carbonate of potash, and the precipitate washed with water, as long as it continues to dissolve carbonate of magnesia, a white, tasteless, soft, elastic powder remains, soluble, according to Dr. Fyfe, in 2493 times its weight of cold, and in 9000 times its weight of boiling water. It dissolves in an aqueous solution of carbonate of potash or soda, and in sulphate and nitrate of potash. When the solutions are heated, the white magnesian salt precipitates again. This white powder, according to the analysis of Berzelius, is a compound of

3 atoms carbonic acid	•	$8 \cdot 25$
4 atoms magnesia .	•	10.0
4 atoms water		4.5
		99.758

22.75§

Berzelius considers it as a compound of

3 atoms carbonate of magnesia,

1 atom quaterhydrate of magnesia.

The magnesia alba of the shops is a mixture of the carbonate and subcarbonate of magnesia in different proportions. It contains the more of the carbonate, and the less of the subcarbonate, the lower the temperature at which the precipitation

<sup>\*</sup> Brooke, Annals of Philosophy (2d series), vi. 375.

<sup>+</sup> Berzelius, Afhandlingar, vi. 21.

<sup>‡</sup> Ann. de Chim, et de Phys. xxix. 285. § Afhandlingar, vi. 26.

of the magnesia is effected. The proportions of the constituents, according to Berzelius, are as follows:

Carbonic acid . 36.58 to 36.4

Magnesia . 41.60 to 43.2

Water . 21.82 to 20.4

100.00 100.0

- 9. Bicarbonate of magnesia. Carbonate of magnesia dissolves in water impregnated with carbonic acid. The solution has a bitter taste, becomes muddy when heated to 167°, but becomes again transparent on cooling. It reddens vegetable blues. This is Dr. Murray's solution of magnesia mentioned above.
- Bergman in 1775.\* It was examined with much care by the indefatigable Vauquelin.† It may be prepared by dissolving carbonate of magnesia in phosphoric acid, and evaporating the solution gradually till the salt crystallizes; but it may be obtained in large regular crystals by a much easier process, first pointed out by Fourcroy. Mix together aqueous solutions of phosphate of soda and sulphate of magnesia in atomic proportions. No change takes place at first; but after some hours crystals of phosphate of magnesia are deposited. Fourcroy describes them as six-sided prisms, with unequal sides. I obtained them in flat four-sided prisms, having a silky lustre, and destitute of taste. According to Vauquelin, they dissolve in 15 times their weight of cold water, and they are still more soluble in hot water. Their constituents, by my analysis, are

14.875

11. Diphosphate of magnesia. According to Riffault, when the preceding salt is boiled in water, a white powder is formed, composed of

10.625

12. Phosphite of magnesia. When phosphite of potash and

\* Opusc. i. 390. † Jour. de l'Ecole Polytechnique.

sulphate of magnesia are mixed, this salt precipitates in white tasteless flocks. They are soluble in 400 times their weight of cold water, and not much more soluble in hot water. The aqueous solution, by spontaneous evaporation, deposits tetrahedral crystals, which effloresce in the air. From the analysis of Fourcroy and Vauquelin, the constituents of this salt appear to be

1 atom phosphorous acid . 3.5%
1 atom magnesia . 2.5
3 atoms water . 3.375
9.375

13. Arseniate of magnesia. This salt may be obtained by mixing rather dilute solutions of sulphate of magnesia and arseniate of soda in atomic proportions. After a few hours, some arseniate of magnesia precipitates in a fine, white, loose state, similar in appearance to hydrate of magnesia. In 24 hours, a number of crystals of the same salt make their appearance. They are small, transparent, four-sided, flat prisms, with very oblique terminations. They constitute tufts of crystals, radiating from a centre, and are formed in the portion of the salt, which has the form of a powder. These crystals are transparent and tasteless, 1000 parts of boiling water dissolve 1.5 of them, and the solution has no sensible taste. Their constituents, by my analysis, are

l atom arsenic acid	•	•	7.25
1 atom magnesia	•	•	2.5
8 atoms water	•	•	9

18.75

- 14. Binarseniate of magnesia. A gelatinous, uncrystallizable matter, soluble in water.
- 15. Biborate of magnesia. This salt occurs in the mountain of Kalkberg, near Luneburgh, and in one or two other spots in small cubic crystals in gypsum. These cubes have usually their edges and four of their angles truncated. It is so hard as to scratch glass, and to strike fire with steel. Its specific gravity is 2.566. When heated, it becomes electric; and, what is singular, the truncated angles are always positively electric, while the opposite entire ones are negative.\*

These crystals are insoluble in water, and not altered by exposure to the air. When heated, they decrepitate: in a red

<sup>\*</sup> Haiiy, Ann. de Chim. ix. 59.

heat they lose their lustre, but do not sensibly diminish in weight. In a white heat they lose 0.005 of their weight. When exposed to the action of a very violent heat, they melt into a yellow-coloured glass. It was first accurately analyzed by Arfvedson, who showed it to be a compound of

2 atoms boracic acid	•	6
l atom magnesia .	•	2.5
		8.5

When magnesia and boracic acid are digested in water, and the solution concentrated, small, irregular crystals are deposited; but their nature has not been determined.

- 16. Silicate of magnesia. No fewer than seven combinations of silica and magnesia occur in the mineral kingdom; namely,
  - (1.) Chrysolite, which is an anhydrous silicate of magnesia.
  - (2.) Nephrite, which is a hydrous silicate, composed of
    - 1 atom water,
    - 1½ atom silicate of magnesia.
  - (3.) Serpentine or hydrous sesquisilicate, composed of
    - 1 atom water,
    - $1\frac{1}{a}$  atom silica,
    - 1 atom magnesia.
  - (4.) Picrocosmine, or anhydrous bisilicate of magnesia.
  - (5.) Schiller spar, or hydrous bisilicate of magnesia.
  - (6.) Pyrallolite, or anhydrous tersilicate of magnesia.
- (7.) Meerschaum, or hydrous tersilicate of magnesia, composed of
  - 4 atoms water,
  - 3 atoms silica,
  - 1 atom magnesia.
- 17. Selenite of magnesia. Selenious acid decomposes carbonate of magnesia, and forms a crystalline matter, which dissolves in boiling water, and deposites crystals in the form of small prisms or four-sided tables. When heated it gives out its water of crystallization, and becomes similar to enamel. It does not melt, nor is it decomposed when heated to redness; but it attacks glass, and gradually makes its way through it.
- 18. Biselenite of magnesia is obtained by dissolving the selenite in selenious acid, and pouring alcohol into the solution. The biselenite precipitates in the form of a pulpy and coherent

mass, which attracts moisture from the atmosphere, is soluble sect. VIII. in water, but does not yield crystals.\*

19. Chromate of magnesia. This salt crystallizes in beautiful, transparent, yellow crystals, which are flat rhomboids, having usually their obtuse angles truncated. It is very soluble in water. Its constituents, by my analysis, are

1 atom chromic acid	•	•	6.5
l atom magnesia	•	•	2.5
2 atoms water	•	•	2.25

11.25

When this salt is exposed to a strong red heat, it is partially decomposed; for it is no longer completely soluble in water.

20. Molybdate of magnesia. This salt may be formed by boiling a mixture of molybdic acid and magnesia in water. It crystallizes in small, white, four-sided prisms, not altered by exposure to the air. The taste is at first bitterish, and then astringent and metallic. It dissolves in from 12 to 15 times its weight of cold water, and when ignited, is converted (by the loss of its water) into a yellowish mass. Its constituents seem to be

1 atom molybdic aci	id	9
1 atom magnesia	•	2.5
4 atoms water .	•	4.5

16.0

- 21. Tungstate of magnesia. When tungstic acid is boiled with carbonate of magnesia, the liquid yields, when evaporated, tungstate of magnesia in small brilliant scales. It is soluble in water, not altered by exposure to the air, and has a taste similar to that of the other species of tungstates. When an acid is dropped in, a white powder or double salt precipitates.
- 22. Oxalate of magnesia. This salt may be formed by double decomposition, or by digesting carbonate of magnesia in a solution of oxalic acid. It is a white tasteless powder, scarcely soluble in water, and not at all in alcohol. When strongly heated, it leaves pure magnesia, without any mixture of charcoal. Its constituents, by my analysis, are

	, j			
1	atom oxalic acid		•	4.5
1	atom magnesia		•	2.5
2	atoms water	•	•	2.25

9.25

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 264.

23. Binoxalate of magnesia. This salt is formed when solutions of binoxalate of potash and sulphate of magnesia are mixed in atomic proportions. When the liquid is concentrated, crystals of binoxalate of magnesia are gradually deposited. They are pretty large flat rectangular four-sided prisms. Its taste is acid, and it reddens vegetable blues. It does not dissolve completely in water; when digested in that liquid a considerable portion of the oxalic acid and some magnesia are dissolved, and oxalate of magnesia remains behind. When heated, oxalic acid readily sublimes. Its constituents, by my analysis, are as follows:

19.375

24. Acetate of magnesia. This salt is easily formed by dissolving magnesia, or its carbonate, in acetic acid. It cannot be made to crystallize. A neutral solution of it was concentrated in vacuo over sulphuric acid. It gradually inspissated into a thick transparent jelly, which was exposed for some time to the heat of the sand bath. Being laid in a cool place, it became solid on the surface, but remained liquid below. Being stirred with a glass rod the whole concreted into a white opaque crystalline looking mass, not unlike loaf sugar. It did not deliquesce though left for a week in a damp room. The taste of this salt is hot and bitter; at first it gives a slight impression of acetic acid, which soon passes off, leaving a very disagreeable taste behind. It is very soluble in water and in alcohol. Its constituents, by my analysis, are

1 atom acetic acid . . 6.25
1 atom magnesia . . 2.5
5 atoms water . . . 5.625

14.375

25. Lactate of magnesia. When the solution of this salt is evaporated to the consistence of a thin syrup and left in a warm place, it shoots into small granular crystals. When hastily evaporated to dryness it furnishes a gummy mass. Alcohol resolves it into two subspecies; neutral lactate which it dissolves, and sublactate which it leaves untouched.\*

<sup>\*</sup> Berzelius, Djurkemien, ii. 437.

26. Formate of magnesia. It crystallizes in fine needles, not sect. VIII. altered by exposure to the atmosphere, and having a sharp and bitterish taste. When exposed to heat they lose no weight, according to Göbel. When strongly heated they swell, become black, and finally leave only carbonate of potash. The salt is soluble in 13 times its weight of cold water, but not in alcohol.

27. Tartrate of magnesia. A white tasteless powder, easily obtained by double decomposition. Its constituents are

•	8.25
•	2.5
•	2.25
	•

13

28. Bitartrate of magnesia. This salt may be formed by dissolving the preceding salt in tartaric acid and crystallizing the solution. The bitartrate is deposited in small acicular crystals. It has a slightly acid taste, and reddens vegetable blues. It is soluble in water. Its constituents are

2 atoms tartaric acid	•	16.5
l atom magnesia .	•	2.5
l atom water .	•	1.125

20.125

- 29. Vinate of magnesia. Though this salt is very little soluble in water, yet a mixture of vinate of soda and sulphate of magnesia lets fall no precipitate in 24 hours.
- 30. Citrate of magnesia. This salt may be formed by dissolving carbonate of magnesia in citric acid. The solution, though evaporated to a thick syrup, does not crystallize, but it gradually assumes the form of a white opaque soft mass, which rises in the vessel like a mushroom.
- 31. Malate of magnesia. Permanent crystals soluble at 60° in 28 times their weight of water.\*
- 32. Fungate of magnesia. Small granular crystals, having very little taste, and easily soluble in water.
- 33. Mucate of magnesia, a white powder, which does not dissolve in water. According to Thenard, there exists also a bimucate of magnesia, but its properties have not been determined.
- 34. Succinate of magnesia. This salt has the form of a white, glutinous, frothy mass, which when dried by the fire attracts moisture from the air and deliquesces.

<sup>\*</sup> Donovan, Phil. Trans. 1815.

- 35. Benzoate of magnesia. This salt forms feather-shaped crystals of a sharp bitter taste, and easily soluble in water.
- 36. Gallate of magnesia. This salt is very little soluble in water, yet gallic acid does not occasion a precipitate in sulphate of magnesia.
- 37. Kinate of magnesia. Crystallizes with difficulty, dissolves readily in water, blackens in the fire, giving out the smell of caramel.
- 38. Bimeconate of magnesia. Fine colourless brilliant needles, having an acid taste, easily soluble in water, but not in alcohol.
- 39. Camphorate of magnesia. This salt may be obtained by boiling an excess of carbonate of magnesia with camphoric acid in water. The filtered solution being sufficiently concentrated yields camphorate of magnesia in flat four-sided prisms. The crystals are translucent, absorb moisture from the atmosphere, and dissolve readily in water. The taste is saline and bitterish, and when heated sufficiently the salt burns with flame. At the temperature of  $36^{\circ}\frac{1}{2}$ , 1 part of it is soluble in  $6\frac{1}{2}$  parts of water. At  $38^{\circ}\frac{3}{4}$ , 100 parts of absolute alcohol dissolve about 1.8 of the salt. The proportion of water in this salt has not been determined. The result of Brandes' analysis would give about

1 ator	n camphoric	acıd	•	12.5
$1\frac{1}{3}$ atom	n magnesia	•	•	3∙33
				15.83

But an error to that amount might easily have been incurred in the analysis.\*

- 40. Suberate of magnesia. This salt may be prepared by the same process as the preceding. It does not crystallize, but may be obtained in the state of a yellowish-white powder, or in translucent crusts and plates. When deprived of its water it assumes the appearance of a white enamel. Its taste is at first soapy, and afterwards bitterish. It absorbs moisture in damp air, but gives it out again in dry air. It is easily soluble in water. At 54° water dissolves its own weight of it.†
- 41. Oleate of magnesia. It may be prepared by mixing hot solutions of oleate of potash and sulphate of magnesia. It is in white clots, translucent, and softens between the fingers.‡
- 42. Cholesterate of magnesia. This salt is insoluble in water.

<sup>\*</sup> Schweigger's Jour. xxxviii. 292. + Brandes, ibid. xxxiii. 92.

<sup>†</sup> Chevreul, sur les corps gras, p. 94.

- 43. Pinate of magnesia. A white powder. When exposed to a heat of 212° it becomes agglutinated together. It dissolves readily in ether. It is soluble also in alcohol.\*
- 44. Silvate of magnesia. This salt dissolves in absolute alcohol and in alcohol of the specific gravity 0.880. When to one part of this last solution two parts of water are added an alcoate of silvate of magnesia falls down of a tarry consistency. This salt is soluble also in ether, oil of turpentine and naphtha.†
- 45. Carbazotate of magnesia. Very long but very fine and indistinct needles, of a light yellow colour, very soluble in water and detonating when heated. ‡
- 46. Urate of magnesia. A white tasteless powder, similar in appearance to uric acid.
- 47. Aspartate of magnesia. Similar in its properties to aspartate of lime.
- 48. Nitrosaccharate of magnesia. A deliquescent salt which does not crystallize, swells much when exposed to heat, and leaves a brown spongy residue like a vegetation.
- 49. Sulphonaphthalate of magnesia. A white salt having a bitterish taste, crystallizing in favourable circumstances, and burning with flame. ¶

#### SECT. IX. -- SALTS OF ALUMINA.

- 1. Most of the salts of alumina are soluble in water, but Characters. few of them are capable of crystallizing.
- 2. They are distinguished by a sweet and astringent taste, in which respect they resemble the salts of yttria and glucina.
- 3. They are not precipitated by oxalate of ammonia nor tartaric acid, which sufficiently distinguishes them from salts of yttria.
- 4. They are not precipitated by prussiate of potash, nor by tincture of nut-galls, in which respects they differ both from the salts of yttria and glucina.
- 5. Phosphate of ammonia, when dropped into a salt of alumina, occasions a white precipitate.
- 6. Hydriodate of potash occasions a white flocky precipitate in a solution of alumina, which speedily becomes yellow and

+ Ibid. p. 400.

|| Braconnot; ibid. xiii. 116.

<sup>\*</sup> Unverdorben, Poggendorf's Annalen, xi. 232.

<sup>‡</sup> Liebig; Ann. de Chim. et de Phys. xxxv. 84.

<sup>§</sup> Plisson; Ann. de Chim. et de Phys. xl. 314.

<sup>¶</sup> Faraday, Annals of Philosophy (2d series), xii. 210.

continues permanent. This is not owing to the excess of acid which the salts of alumina usually contain, for the yellow colour does not disappear on the addition of carbonate of ammonia.

- 7. If sulphuric acid, and then sulphate of potash be added to a salt of alumina, and the mixture be set aside, octahedral crystals of alum speedily make their appearance in it.
- 8. When nitrate of cobalt is mixed with a mineral containing alumina and the mixture is exposed to the action of the blow-pipe it acquires a fine blue colour, which becomes deeper without losing its colour by an additional quantity of cobalt. The colour is only seen distinctly by daylight and after the assay is cold. This method of proceeding may be followed successfully with most of the salts of alumina.
- 1. Sulphate of alumina. This salt may be formed by digesting hydrated alumina in dilute sulphuric acid till the acid is completely saturated. A very long continued digestion is necessary for this purpose. When the solution is concentrated in vacuo over sulphuric acid it gradually congeals into a beautiful white, soft, light semitransparent mass, which may be dried on blotting paper, and is not altered by exposure to the atmosphere. It reddens vegetable blues. Its taste is astringent and sour with an impression of sweetness. It is very soluble in water, and the acid and water which it contains may be driven off by heat. Its constituents, by my analysis, are:

ıcid	•	•	5
•		•	2.25
•	•	•	7.875
			15.125
	ecid		

2. Trisulphate of alumina. This is a fine white aluminous looking mineral found in Sussex and near Halle, and distinguished by mineralogists by the name of aluminite. It is tasteless and insoluble in water; but it may be dissolved in acids. Its constituents, as is obvious from the analysis of Stromeyer, are as follows:

1 atom sulphuric ac	id,	•	•	5
3 atoms alumina,	•	•	•	6.75
9 atoms water,	•	•	•	10.125
-				
				21.875

3. Subsulphate of alumina. When we precipitate sulphate of alumina by means of ammonia or carbonate of soda, we can-

not deprive the alumina, however frequently we wash it, of all its sulphuric acid. It continues a compound of

1 atom sulphuric acid 30 atoms alumina.

Whether this precipitate be actually a compound of alumina and sulphuric acid in these proportions, or whether it be a mixture of alumina and trisulphate of alumina, we have no means of determining.

4. Sulphite of alumina. This salt was first formed by Berthollet; it has been described by Fourcroy and Vauquelin.

When formed by the usual process it remains in the state of a white powder, and does not crystallize though dissolved in an excess of acid.

It is white and soft, and has an earthy and sulphureous taste. It is insoluble in water. When exposed to the air, it is gradually converted into sulphate. Its solution in sulphurous acid undergoes this change much more rapidly. When heated, its acid is disengaged, and the alumina remains behind, mixed however with a small proportion of sulphate of alumina.

- 5. Hyposulphite of alumina. Mr. Herschell did not succeed in obtaining this salt. When oxalate of alumina was dropped into hyposulphite of lime no precipitate fell. He assures us that oxalate of alumina occasions no precipitate in muriate or nitrate of lime, any more than in hyposulphite.\*
- 6. Hyposulphate of alumina. This salt was obtained by mixing solutions of hyposulphate of barytes and sulphate of alumina. The filtered solution was concentrated in vacuo over sulphuric acid. A white mass was obtained, which, however, when dissolved in water, was copiously precipitated by chloride of barium. It would appear from this, that this salt cannot be brought into a dry state without undergoing decomposition.+
- 7. Nitrate of alumina. I have not been able to obtain this salt by digesting nitric acid on hydrate of alumina; but it is described by chemists as composed of soft white crystalline plates. Its taste is acid and astringent and it reddens vegetable blues. It dissolves readily in water and alcohol, and deliquesces when exposed to the air. According to Bucholz's analysis, the constituents (abstracting the water) are

<sup>\*</sup> Edin. Phil. Jour. i. 21. † Heeren; Poggendorf's Annalen, vii. 180.

# Class I. This approaches

1 atom nitric acid	•		9
l atom alumina .	•	•	2.25
			11.05

But it is doubtful how far we can depend upon the accuracy of this analysis.

8. Dinitrate of alumina. This salt may be formed by digesting hydrate of alumina in dilute nitric acid till the acid refuses to take up any more. When the solution is concentrated and set aside it concretes into a white solid matter, which may be dried by pressure between folds of blotting paper. Thus prepared it is a white crystalline powder, very soluble in water, and reddening vegetable blues. Its taste is astringent and sweet, with an impression of acidity. Its constituents, by my analysis, are

1 atom nitric acid	•		6.75
2 atoms alumina	•	•	4.5
10 atoms water	•	•	11.25
			99.5

9. Trisnitrate of alumina. When the preceding salt is heated on the sand-bath till it loses its liquid form and forms a white dry crust it is converted into trisnitrate. It is nearly insoluble in water, and does not deliquesce when exposed to the air. Its constituents, by my analysis, are

1 atom nitric acid	•	•	6.75
3 atoms alumina	•	•	6.75
6 atoms water .	•		6.75
			20.25

- 10. Carbonate of alumina. Saussure has shown that water saturated with carbonic acid is capable of dissolving alumina; but this combination is destroyed by simple exposure to the air. Carbonate of alumina, then, cannot exist in a dry state. What had been considered formerly as a dry carbonate is a triple compound of alumina, carbonic acid, and the alkali employed in precipitating the alumina.\*
- 11. Phosphate of alumina. This salt may be obtained by mixing solutions of alum and phosphate of soda in the atomic proportions. No precipitate appears at first; but if the mix-

Sect. IX.

ture be heated, a white powder falls, which is the phosphate of alumina. It is tasteless and insoluble in water; but reddens vegetable blues powerfully. Its constituents seem to be

1	atom phosphor	ric a	cid	•	4.5
	atom alumina		•	•	2.25
$3\frac{1}{2}$	atoms water	•	•	•	3.9375
_					

10.6875

- 12. Biphosphate of alumina. When the preceding salt is dissolved in phosphoric acid, and the solution concentrated, a gummy mass is obtained, which may be fused into a transparent bead, and which is probably a biphosphate.
- 13. Diphosphate of alumina. The mineral called wavellite, appears, from the analysis of Fuchs and Berzelius, to be a hydrated diphosphate of alumina, composed of

1 atom phosphoric	acid	•	4.5
2 atoms alumina	•		4.5
3 atoms water	•	•	3.375

12.375

- 14. Phosphite of alumina. This salt does not crystallize, but forms a gelatinous mass, which, when heated, gives out phosphuretted hydrogen gas, and is converted into phosphate of alumina.
- 15. Arseniate of alumina. This salt may be obtained by mixing together solutions of alum and arseniate of soda in the atomic proportions. It is a white, tasteless, insoluble powder, not unlike phosphate of lime; but strongly reddening vegetable blues. Its constituents are

I atom arsenic acid I atom alumina	•	•	7·25 2·25
6 atoms water	•	•	6.75

16.25

- 16. Binarseniate of alumina. It may be obtained by dissolving the preceding salt in arsenic acid, and concentrating the solution sufficiently. It dissolves in water, and does not crystallize.
- 17. Borate of alumina. When solutions of alum and borax are mixed, the liquid deposites white, pearly plates, very soft, and scarcely soluble in water. This salt has not been analyzed. Analogy would lead us to consider it as a biborate.
  - 18. Silicate of alumina. No fewer than nine different

- minerals occur which are true saline combinations of silica and alumina. These are
  - (1.) Andaluzite, or disilicate of alumina.
  - (2.) Bucholzite, or silicate of alumina.
  - (3.) Cyanite, or subsesquisilicate, composed of

l atom silica,

11 atom alumina.

(4.) Halloylite, or hydrous silicate, composed of

1 atom silicate of alumina,

1 atom water.

(5.) Pholerite, composed of

14 atom silicate of alumina

1 atom water.

- (6.) Nacrite, or anhydrous bisilicate of alumina.
- (7.) Fuller's earth, or hydrous bisilicate, composed of l atom bisilicate of alumina, l atom water.
- (8.) Lenzinite, or hydrous tersilicate, composed of 1 atom tersilicate of alumina, 3 atoms water.
- (9.) Quatersilicate of alumina; a yellowish-white, fibrous mineral from Mexico.
- 19. Selenite of alumina. This salt is obtained by precipitating muriate of alumina by biselenite of ammonia. It is a white powder, insoluble in water. When heated, it allows first its water, and then its acid to escape.
- 20. Biselenite of alumina is obtained by dissolving the selenite or hydrate of alumina in selenious acid. It has an astringent taste, and yields by evaporation a transparent matter similar to gum.\*
- 21. Chromate of alumina. A yellow salt, soluble in water, and not capable of crystallizing.
  - 22. Tungstate of alumina. An insoluble white powder.
- 23. Oxalate of alumina. Oxalic acid dissolves hydrate of alumina with facility. The saturated solution is transparent and colourless; it has a sweet and astringent taste, and reddens vegetable blues. By evaporation we obtain oxalate of alumina in a semitransparent, amber-coloured crust, very similar in appearance to gum or albumen dried in a low heat. It dissolves with facility in water, and may be exposed to the air without absorbing moisture. Its constituents are

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. x. 365.

1 atom oxalic acid	.•	•	4.5
l atom alumina	•	•	2.25
3 atoms water	•	•	3.375

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10.125

24. Acetate of alumina. This salt may be obtained by digesting hydrated alumina in cold acetic acid, till the acid is saturated. When the solution is left to spontaneous evaporation in a warm place, the salt shoots into long, transparent, four-sided prisms. Its taste is sweet and astringent, with something of the flavour of acetic acid. It dissolves readily in water, and reddens vegetable blues. Its constituents are

1 atom acetic acid		•	6.25
1 atom alumina	•		2.25
1 atom water	•	•	1.125

9.625

Gay-Lussac first observed that when a solution of this salt in water is heated, it deposites one-half of its alumina, and is converted into a binacetate, but on cooling it again takes up the portion thrown down, and becomes neutral as at first.\*

- 25. Lactate of alumina. A salt not altered by exposure to the air, and having the appearance of gum.+
- 26. Formate of alumina. A gummy matter, incapable of crystallizing, taste sharp and astringent, not very soluble in water. From Göbel's observations, it would appear that its aqueous solution when heated deposites one half of its alumina as is the case with the solution of acetate of alumina.
- 27. Tartrate of alumina. Tartaric acid dissolves hydrate of alumina with facility. The saturated solution has an acid, astringent, and sweet taste. When evaporated to dryness it leaves a white, semitransparent, viscid mass, having a slight shade of yellow, and very like gum arabic in appearance. On exposure to the air it becomes brittle, but still continues to redden vegetable blues. Its constituents are

1 atom tartaric acid		•	8.25
l atom alumina		•	2.25
l atom water .	•	•	1.125

11.625

28. Citrate of alumina. When there is an excess of alumina

<sup>\*</sup> Ann. de Chim. lxxiv. 193. † Braconnot, ibid. lxxxvi. 88.

- the salt is insoluble; when of acid, a gummy matter is obtained, soluble in water.
  - 29. Malate of alumina. This salt is almost insoluble in water.\* Of course it precipitates when malic acid is dropped into a solution containing alumina. Mr. Chenevix has proposed this acid to separate alumina from magnesia; which earths, as is well known, have a strong affinity for each other.+
  - 30. Fungate of alumina. A gummy mass, which does not crystallize.
    - 31. Mucate of alumina. A white powder insoluble in water.
  - 32. Succinate of alumina. This salt, according to Wenzel, crystallizes in prisms, and is easily decomposed by heat.
  - 33. Benzoate of alumina. This salt forms dendritical crystals. It has a sharp bitter taste, is soluble in water, and deliquesces when exposed to the air.
  - 34. Gallate of alumina. When a small portion of alumina is mixed with the infusion of nut-galls, it separates the whole of the tan and extract, and leaves the liquid limpid and of a very pale yellowish green colour. This liquid, by spontaneous evaporation, yields small transparent prismatic crystals, which, according to Davy, are supergallate of alumina. They afford the only instance of a gallate capable of existing in the state of crystals. The quantity of alumina is very small; too small to disguise the properties of the acid.
  - 35. Camphorate of alumina. To prepare this salt, alumina, precipitated by means of ammonia, and well washed, is to be mixed with water, and crystals of camphoric acid added. mixture is then to be heated, filtered, and concentrated by evaporation. This salt is a white powder, of an acid bitterish taste, leaving on the tongue, like most of the aluminous salts, a sensation of astringency. Water at the temperature of 60° dissolves about  $\frac{1}{\sqrt{0.0}}$ th part of its weight of this salt. water dissolves it in considerable quantities, but it precipitates again as the solution cools. Alcohol, while cold, dissolves it very sparingly; but when hot it dissolves a considerable quantity of it, which precipitates also as the solution cools. salt undergoes very little alteration in the air, but it rather parts with than attracts moisture. Heat volatilizes the acid; and when the salt is thrown on burning coals, it burns with a blue flame.

<sup>\*</sup> Ann. de Chim. xxviii. 921.

<sup>†</sup> Braconnot.

Ann. de Chim. xxvii. 34.

<sup>+</sup> Ibid.

<sup>§</sup> Verwandt. p. 243.

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- 36. Suberate of alumina. This salt does not crystallize. When its solution is evaporated by a moderate heat in a wide vessel, the salt obtained is of a yellow colour, transparent, having a styptic taste, and leaving an impression of bitterness on the tongue. When too much heat is employed, it melts and blackens. It reddens the tincture of turnsole, and attracts moisture from the air. Before the blow-pipe it swells up, the acid is volatilized and decomposed, and nothing remains but the alumina.\*
- 37. Cholesterate of alumina. When cholesterate of potash is mixed with a solution of alum a precipitate falls, at first of a beautiful red colour, but when dried the colour becomes much deeper.
- 38. Pinate of alumina. Pinate of potash throws this salt down from alum. It melts when heated, is insoluble in water and alcohol, but dissolves in ether and in oil of turpentine, by which last substance it undergoes partial decomposition.
- 39. Urate of alumina. A white powder, scarcely distinguishable by its aspect from uric acid.

#### SECTION X. -- SALTS OF GLUCINA.

The salts of glucina have been examined equally imperfectly with the salts of yttria.

- 1. The salts of glucina are much more soluble in water than characters. those of yttria, and a smaller number of them seem susceptible of crystallizing.
- 2. The salts of glucina are not precipitated by oxalate of ammonia or tartrate of potash, which sufficiently distinguishes them from salts of yttria.
- 3. Prussiate of potash occasions a white precipitate when dropped into the solution of a salt of glucina.
- 4. Infusion of nut-galls occasions a yellow precipitate, which acquires a purplish tinge if any iron be present.
- 5. The sulphate of glucina does not crystallize, nor do crystals of alum form in it when sulphate of potash is mixed with the solution.
- 6. When a salt of glucina is mixed with a little nitrate of cobalt and exposed to the action of the blow-pipe, it becomes black or dark gray.
- 1. Trisulphate of glucina. When glucina is dissolved in sulphuric acid till no more is taken up, and the liquid thus obtained

<sup>\*</sup> Ann. de Chim. xxiii. 55. † Unverdorben.

is evaporated to dryness and washed with alcohol, we obtain a bisulphate of glucina. If this bisulphate be boiled with carbonate of glucina and water, and the solution thus obtained be set aside, a precipitate falls, which is a trisulphate of glucina. It is a white powder, composed, according to the analysis of Berzelius, of

 1 atom sulphuric acid
 .
 5

 3 atoms glucina
 .
 9.75

 3 atoms water
 .
 3.375

 18.125

2. Subsesquisulphate of glucina. When the liquid from which the trisulphate has fallen is concentrated, we obtain a translucent, gummy mass, which becomes brittle when cold, but soft and doughy at the temperature of 212°. When this substance is dried so as to drive off the water, it is changed into a spongy shining substance, insoluble in water, and composed, according to the analysis of Berzelius, of

1	atom	sulphuric	acid	•	5
$1\frac{1}{2}$	$\mathbf{atom}$	glucina	•	•	4.875
					9.875

3. Sulphate of glucina. This salt may be obtained by nearly the same process as the preceding. It has a sweet taste, is soluble in water, and is composed (abstracting the water) of

1 atom sulphuric acid	•	5
1 atom glucina .	•	3.25
		8.25

4. Bisulphate of glucina. It is obtained by digesting glucina in sulphuric acid. The solution by evaporation yields small needle-form crystals, the figure of which has not been ascertained.

It has a very sweet and somewhat astringent taste. It is soluble in water; the solution readily assumes the consistence of a syrup, but does not crystallize. When heated, it undergoes the watery fusion, loses its water, and falls to powder. At a red heat it is decomposed completely, the acid is driven off, and the earth remains in a state of purity. The infusion of nut-galls, when dropped into the solution of this salt, occasions a yellowish white precipitate.

The constituents of this salt, by my analysis, are as follows: seet. x.

2 atoms sulphuric acid . 10
1 atom glucina . . 3.25
5 atoms water . . 5.625

18.875

5. Nitrate of glucina. This salt was first described by Vauquelin. It is prepared by saturating nitric acid with glucina. When this solution is evaporated by means of a low heat, the salt gradually assumes the form of a powder, but cannot be obtained in the state of crystals.

Its taste is sweet and astringent. It is exceedingly soluble in water, so much so indeed, that it is very difficult to obtain it in a dry state. When evaporated, it becomes thick and glutinous like honey. When exposed to the air, it attracts moisture very rapidly. When heated it readily melts, and if the heat be increased, the acid escapes, and leaves the earth in a state of purity. When tincture of nut-galls is dropped into a solution of this salt, a yellowish-brown precipitate immediately appears. Nitrate of glucina may be readily distinguished from nitrate of alumina by this property.

- 6. Carbonate of glucina. This salt has been examined only by Vauquelin. It may be prepared by precipitating glucina from its solution in acids by an alkaline carbonate, and washing the precipitate sufficiently with pure water. It is in the state of a white soft powder, which has a greasy feel. It has no taste, and is exceedingly light. It is insoluble in water, not altered by exposure to the air, easily decomposed, and its acid driven off by the application of heat. It loses half of its weight in a red heat.
- 7. Phosphate of glucina. This salt has been examined only by Vauquelin. He obtained it by pouring phosphate of soda into the solution of glucina in sulphuric, nitric or muriatic acid. The phosphate of glucina is precipitated in the state of a white powder. It does not crystallize. It is tasteless, insoluble in water, unless it contains an excess of acid, and not liable to be altered by exposure to the air. When heated strongly, it melts into a transparent glass.
- 8. Biphosphate of glucina. Obtained by digesting the preceding salt in an aqueous solution of phosphoric acid.
  - 9. Arseniate of glucina is a white powder insoluble in water.
- 10. Binarseniate of glucina is obtained when the preceding salt is digested in an aqueous solution of arsenic acid.

11. Silicate of glucina. This salt has not been examined; but the rare mineral called euclase is a compound of

2 atoms silicate of alumina, 1 atom silicate of glucina.

- 12. Selenite of glucina. The neutral salt is a white insoluble powder. The biseleniate is soluble. When evaporated it gives a gummy looking mass. Heat decomposes both of these salts.\*
- 13. Chromate of glucina. Glucina thrown down by carbonate of potash is dissolved very slowly by concentrated chromic acid. The solution has a yellow colour, and does not seem capable of crystallizing.†
- 14. Oxalate of glucina. A brittle translucent gummy mass, which does not crystallize, has a sweet taste, and is soluble in water.
- 15. Acetate of glucina. Acetate of glucina is sweet and astringent, has an excess of acid, and does not crystallize, but forms a gummy mass in thin transparent plates, soluble in water, and still acid.‡ Acetic acid does not dissolve glucina heated to redness.
- 16. Tartrate of glucina. Crystallizes with difficulty by spontaneous evaporation. Very soluble in water.§
- 17. Citrate of glucina. Does not crystallize, but assumes the form of gum. $\parallel$
- 18. Succinate of glucina. Ekeberg has announced, that glucina is precipitated from its solution in acids by the succinates. The succinate of glucina is of course insoluble, or nearly so.¶
- 19. Benzoate of glucina. The salts of glucina, when concentrated, are also precipitated by benzoate of ammonia. The precipitate consists of white flocks.

### SECTION XI.—SALTS OF YTTRIA.

The greater number of the salts which yttria is capable of forming with acids still continue unknown.

Characters.

- 1. A considerable number of the salts of yttria are insoluble in water, and have not therefore been obtained in the state of crystals.
  - 2. Yttria may be precipitated from its solutions in acids by
    - \* Berzelius, Ann. de Chim. et de Phys. ix. 265.
    - † John, Annals of Philosophy, iv. 425.
    - † Vauquelin, Ann. du Mus. d'Hist. Nat. xv. 9.
    - § Vauquelin. | Ibid. ¶ Ann. de Chim. xliii. 277.

phosphate of soda, carbonate of soda, oxalate of ammonia, and tartrate of potash.

3. It is precipitated likewise in a white chalky state by

prussiate of potash.

4. The alkaline carbonates throw down a white precipitate when dropt into solutions of yttria in acids, but the precipitate is redissolved by adding an excess of the carbonate. In this property yttria agrees with glucina.

5. The salts of yttria have fully as sweet a taste as those of glucina, but they are also astringent. The taste may be compared to that which would be produced by mixing together

solutions of glucina and alumina.

1. Sulphate of yttria. This salt was first formed by Gadolin, and afterwards it was examined with more precision by Ekeberg,\* Vauquelin,+ and Klaproth.‡ A considerable number of the salts of yttria were prepared, examined, and analyzed in my laboratory during the winter 1830–31 by Dr. Steel. I shall make use of his observations, which he has put into my possession in order to render my account of the salts of yttria more correct.

Sulphuric acid acts with considerable energy on anhydrous yttria, a good deal of heat being evolved. The salt crystallizes in doubly oblique prisms, and also in acute rhomboids. The taste of the salt is sweet and astringent. It is insoluble in alcohol. At 65° 100 parts of water dissolve 8 parts of the salt. The specific gravity of the crystals is 2.565. The salt reddens vegetables. It may be exposed to a gentle heat without decomposition. But in a high temperature it is partly decomposed. It was subjected to three successive analyses by Dr. Steel. The results obtained were as follows:

			1		2		3
Sulphuric	acid	 •	5.00	•	5.00		5.00
Yttria	•	•	$5 \cdot 45$	•	<b>5.59</b>	•	5.54
Water	•	•	3.19		2.31		3.04

Berzelius had previously determined the ratio of the acid and yttria to be

Sulphuric	acid	•	•	5
Yttria	•	•	•	5.4012

The composition of the salt from these analyses is obviously

<sup>\*</sup> Crell's Annals, 1799, ii. 68.

<sup>‡</sup> Beitrage, iii. 67.

<sup>†</sup> Ann. de Chim. xxxvi. 156.

<sup>§</sup> Annals of Philosophy, iii. 359.

1 atom sulphuric	acid	•	•	5
l atom yttria	•		•	5.5*
2 atoms water	•	•	•	2.25
				12:75

Dr. Steel found that when 12.75 grains of this salt were mixed with 8.875 grains of oxalate of ammonia, the residual liquid (after the precipitation of the oxalate of yttria) was neither altered by sulphate of yttria nor oxalate of ammonia. Yet it retained about 0.32 grain of yttria, owing probably to the oxalate of yttria not being quite insoluble.

Dr. Steel did not succeed in obtaining a bisulphate of yttria.

- 2. Disulphate of yttria is obtained, according to Berzelius, when the preceding salt is exposed to a red heat, or when its aqueous solution is mixed with ammonia. It is a white powder insoluble in water.
- 3. Nitrate of yttria. This salt was first formed by Mr. Ekeberg: it was afterwards examined by Vauquelin. It may be prepared by dissolving yttria in nitric acid. The solution has a sweet astringent taste, and in most of its properties agrees with nitrate of glucina. Like it, this salt can scarcely be obtained in the state of crystals. If, during the evaporation, a heat somewhat too strong be applied, the salt becomes soft, and assumes the appearance of honey, and on cooling becomes hard and brittle like a stone. When exposed to the air, it very soon attracts moisture, and deliquesces. When sulphuric acid is poured into this solution, crystals of sulphate of yttria are instantly precipitated.†

When nitric acid is poured upon yttria no immediate action takes place, but when gently heated the yttria dissolves at once with the evolution of deutoxide of azote. It appears to yield the rudiments of crystals in prisms. When gently heated it melts into a beautiful transparent glass; but a very moderate heat decomposes it. From its great deliquescing powers it is scarcely possible to dry it. Dr. Steel concluded from his experiments that the constituents of the crystals, supposing them dry, are

l atom nitric acid		•	6.75
1 atom yttria .	•	•	5.50
2 atoms water .	•	•	2.25

14.5

<sup>\*</sup> In volume i. p. 442, I have adopted 5.25 as the atomic weight of yttria; but the analytical results of Dr. Steel agree best with 5.5 for the atomic weight of that earth.

<sup>+</sup> Ann. de Chim. xxxvi. 156.

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4. Carbonate of yttria. This salt may be formed by precipitating yttria from its solution in acids by means of an alkaline carbonate. It is a white, tasteless, insoluble powder, but soluble in the alkaline carbonates. When a solution of yttria in an alkaline carbonate is heated, the yttria is precipitated in the state of a carbonate, but is again dissolved when the solution cools. Its constituents, from the analysis of Dr. Steel, seem to be

1 atom	carbonic	acid	•	•	2.75
1 atom	yttria		•	•	$5 \cdot 5$
1 atom water	•		•	1.125	
					9.375

Dr. Steel did not succeed in obtaining a solution of carbonate of yttria in water by means of a current of carbonic acid gas. It would appear from this that a bicarbonate of yttria does not exist.

5. Subsesquiphosphate of yttria. When solutions of phosphate of soda and sulphate of yttria are mixed together, gelatinous flocks are precipitated, having much the appearance of hydrate of alumina. After ignition it still retains its opalescent appearance, but becomes more compact and of a vitreous lustre. From the analysis of Dr. Steel, its constituents were found to be

Phosphe	oric a	acid	•	•	4.477
Yttria	•	•			8.25
Water	•	•	•	•	2.8

This corresponds with

1 atom phosphori	e acid	•	4.5
1 atom yttria	•		8.25
$2\frac{1}{2}$ atoms water	•	•	2.8125
			15.5625

This is similar to the phosphate of yttria found native, and recently analyzed by Berzelius.

- 6. Phosphate of yttria. Gadolin describes this salt as a white powder, not fusible before the blow-pipe, and almost insoluble in water. But he does not inform us how it was obtained, nor whether it was analyzed.
- 7. Arseniate of yttria. When yttria is dissolved in arsenic acid, and the solution boiled, arseniate of yttria precipitates in the state of a white powder.\* Arseniate of potash precipitates yttria from acids.†

<sup>\*</sup> Ekeberg, Crell's Annals, 1799, ii. 70. † Klaproth's Beitrage, iii. 76.

- 8. Borate of yttria. This salt precipitates when solutions of borax and sulphate of yttria are mixed together. Before the blow-pipe it fuses into a bead.\*
- 9. Chromate of yttria. Chromic acid dissolves yttria cold in considerable quantity and with effervescence. The solution has an astringent and pungent taste, and, like most of the chromates, has an orange-red colour passing into yellow. The solution is quite neutral. When evaporated, it forms dendrites consisting of prisms and cubes. It is very soluble in water.+
- 10. Selenite of yttria. When an alkaline selenite is dropt into a solution of yttria, a white precipitate falls in large flocks, which do not dissolve in an excess of selenious acid. When dry it has the appearance of a white powder. On exposure to heat it first parts with its water and then with its acid.‡
- 11. Oxalate of yttria. This salt is obtained when oxalate of ammonia is dropt into sulphate of yttria. A snow-white powder falls, which is tasteless and insoluble in water. Its composition, according to the analysis of Dr. Steel, was

1 atom oxalic a	cid	•	•	4.5
1 atom yttria	•	•	•	5.5
2 atoms water	•	•	•	2.25
				12.25

12. Sesqui-oxalate of yttria. When, instead of dropping oxalate of ammonia into sulphate of yttria, we reverse the process, and drop sulphate of yttria into oxalate of ammonia, the precipitate has the same appearance as in the preceding case; but the salt formed appears, from Dr. Steel's analysis, to be a sesqui-oxalate, composed of

$1\frac{1}{2}$	atom	oxalic acid	•	•	6.75
1	atom	yttria	•	•	5.5
					12.25

The result of two successive analyses was

Oxalic a	cid	•	•	•	6
Yttria		•	•	•	5.5

So that about  $\frac{1}{9}$ th of the oxalic acid was wanting to make up the atomic amount.

13. Dinoxalate of yttria. When yttria is precipitated from

<sup>\*</sup> Gadolin. + John, Annals of Philosophy, iv. 426.

<sup>‡</sup> Berzelius, Ann. de Chim. et de Phys. ix. 265.

a solution containing an excess of acid by means of oxalic acid, there is occasionally obtained a dinoxalate, which seems to be anhydrous; for Dr. Steel analyzed it, and obtained

Sect. XI,

1 atom oxalic acid .	•	4.5
2 atoms yttria .	•	11.0
½ atom (nearly) water	•	·279
_		
		15.779

14. Acetate of yttria. Yttria dissolves readily in acetic acid, and the solution yields by evaporation crystals of acetate of yttria. The crystals are beautiful rhombs, having an amethyst colour, and not altered by exposure to the air. Its constituents, according to the analysis of Dr. Steel, are as follows:

1 atom acetic acid	•	•	6.25
1 atom yttria	•	•	5.5
3 atoms water	•	•	3.375
			15.105

15. Tartrate of yttria. This salt may be obtained by precipitating sulphate of yttria by tartrate of potash. It is a beautiful, light, white powder. Its constituents, according to the analysis of Dr. Steel, are

1 atom t	artaric	acid			8.25
1 atom y	<i>t</i> tria		•	•	<b>5·5</b>
1 atom v	vater		•	•	1.125

14.875

- 16. Succinate of yttria. Yttria is not precipitated from its solution in acids by the succinates, according to Ekeberg.\* This, however, must be understood with some limitation; for as the succinate of yttria is but sparingly soluble in water, it precipitates in crystals, if a concentrated solution of an alkaline succinate be mixed with a saturated solution of yttria in an acid. Thus, when the succinate of soda is dropped into concentrated muriate or acetate of yttria, small cubic crystals fall, which are succinate of yttria.+
- 17. Benzoate of yttria. When benzoate of ammonia is dropped into a solution of sulphate of yttria (unless it be very dilute) a white precipitate falls, which is benzoate of yttria. It is scarcely, if at all, soluble in water.

<sup>\*</sup> Ann. de Chim. xliii. 277.

<sup>†</sup> Klaproth's Beitrage, iii. 76.

### SECTION XII. - SALTS OF PROTOXIDE OF CERIUM.

For the facts respecting this genus of salts at present known, we are chiefly indebted to the labours of Klaproth, Hisinger, Berzelius, and Vauquelin. Several of these salts of cerium were subjected to a very minute and accurate investigation in my laboratory, by Dr. Steel, during the winter of 1830-31.

The salts of protoxide of cerium possess the following properties:

- 1. They are usually of a light flesh-red colour, or sometimes nearly white.
  - 2. Their solutions in water have a sweet taste.
- 3. Hydrosulphuret of potash occasions only a white precipitate consisting of the oxide of cerium. Sulphuretted hydrogen occasions no precipitate.
- 4. Prussiate of potash occasions a snow-white precipitate, soluble in nitric and muriatic acids.
- 5. Gallic acid and the infusion of nut-galls occasion no precipitate.
- 6. The oxalate of ammonia occasions a white precipitate, which is soluble in nitric and muriatic acids.
- 7. Arseniate of potash when dropped into solutions of salts of cerium occasions a white precipitate. Tartrate of potash occasions no precipitate.
- 1. Sulphate of cerium.\* This salt is formed by dissolving peroxide of cerium in sulphuric acid, and adding a little muriatic acid, and digesting. Chlorine gas is evolved, and the solution becomes colourless, and when sufficiently concentrated it yields prismatic crystals of sulphate of protoxide of cerium. Or the salt may be formed by saturating dilute sulphuric acid with protoxide of cerium, and concentrating the solution sufficiently. It has a flesh-red colour, an agreeably sweet and astringent taste, and a specific gravity of about 2.5. 100 parts of water at the temperature of 60° dissolve 6.47 parts of this salt. When heated it becomes white and opaque; but cannot be rendered anhydrous without losing a portion of its acid. By two or three crystallizations it is rendered quite neutral. Dr. Steel subjected this salt to three successive analyses, the results obtained were as follows:

<sup>\*</sup> When the name of the metal is placed after the generic appellation of the salt, it denotes that the salt contains the protoxide of the metal. Thus sulphate of iron is sulphate of protoxide of iron, and sulphate of cerium is sulphate of protoxide of cerium.

	Sect.	XII.
-		

		1 <b>4·6</b>		² 6·52		3 6·42
•	•	6.58		9.27	•	8.893
•	•	1.9	•	4.67	•	4.20
		13.08*		20·46†		19·513±
	•		6.58	6.58 1.9 .	6·58 . 9·27 1·9 . 4·67	6·58 . 9·27 1·9 . 4·67 .

If we reduce these numbers to what they would be if the sulphuric acid in each analysis were 5, or an atom, we have

			i		2		3
Sulphuric acid	•	•	5.00	•	5	•	5
Peroxide of cerium	•	•	7.15		<b>7·1</b>	•	6.92
Water	•	•	2.06	•	3.5	•	3.25
			14.21	•	15.6		15.17
Salt analyzed	•		13.85	•	15.33	•	14.79

Increase of weight . . 0.36 . 0.27 . 38

The reason of the increase of weight is, that during the analysis the protoxide of cerium has been changed into peroxide. From Hisinger's experiments we know that the peroxide of cerium contains  $1\frac{1}{2}$  atom oxygen, while the protoxide contains only 1 atom. The increase in the above analysis ought to have amounted to 0.5. It is somewhat less than this, owing to the unavoidable loss sustained in all such analyses, and also to the difficulty of rendering the salt anhydrous, without driving off some of its acid. The mean weight of the peroxide of cerium in the three analyses is 7.05. From this it follows that the atomic weight of peroxide of cerium is 7. Consequently that of protoxide of cerium must be 6.5. And the constitution of sulphate of cerium must be

1 atom sulphuric acid	•	•	5
1 atom protoxide of cerium	•	•	6∙5∮
3 atoms water	•	•	3.375
	_		14.875

- 2. Disulphate of cerium. An insoluble white powder, obtained by precipitating sulphate of cerium by ammonia. Its
- \* The weight of salt analyzed was 12.75 grains. Increase of weight 0.33. gr.
  - + Salt analyzed, 20 grains. Increase 0.46 gr.
  - ‡ Salt analyzed, 19 grains. Increase 0.513.
- § My own experiments gave the atom of protoxide of cerium 7.25. See First Principles, i. 380. But perhaps they were made on too small a scale to be implicitly depended on.

constituents, according to the analysis of Dr. Steel, are as follows:

1 atom sulphuric acid	•	•	5
2 atoms protoxide of cerium	•	•	13
2 atoms water	•	•	2.25
			20.25

The quantity of water actually obtained was 2.1.

- 3. Nitrate of cerium. The solution of this salt is colourless, crystallizes with difficulty, retains an excess of acid, and has an austere and sweet taste.
- 4. Carbonate of cerium. Carbonic acid combines readily with the protoxide of cerium. The easiest way of forming the carbonate is to precipitate oxide of cerium from its solution by means of an alkaline carbonate. The precipitate is granular, of a silvery whiteness, and insoluble in water acidulated with carbonic acid. From the analysis of Klaproth, there is reason to believe that the constituents of this salt are

1 atom carbonic acid	•	•	$2 \cdot 75$
1 atom protoxide of cerium	•	•	6.5
l atom water	•	•	1.125
			10:375

5. Subsesquiphosphate of cerium. When a solution of protoxide of cerium is mixed with phosphate of soda, a white powder falls which is tasteless and insoluble in water, but is slightly soluble in nitric and muriatic acids. By exposure to a red heat its colour is changed to a greenish-yellow; but it does not undergo fusion. Its constituents, according to the analysis of Dr Steel, are

1 atom phosphoric acid	•	•	4.5
$1\frac{1}{2}$ atom protoxide of cerium	•	•	9.75
			14.25

The actual result of the analysis was

Phosphoric acid	•	•	4.5 = 1	atom
Protoxide of cerium	•	•	10.22 = 1.57	23 atom

This is the only phosphate of cerium hitherto examined.

- 6. Arseniate of cerium. Obtained by saturating arsenic acid with protoxide of cerium by digestion. It is a white powder not soluble in water, and not hitherto subjected to analysis.
  - 7. Binarseniate of cerium is obtained when the preceding

salt is digested in arsenic acid. It does not crystallize, but sect. XII. when concentrated assumes the form of a jelly.\*

- 8. Selenite of cerium. A white powder insoluble in water.+
- 9. Biselenite of cerium is obtained when the preceding salt is dissolved in selenious acid.t
- 10. Chromate of cerium. A yellow powder insoluble in water.§
- 11. Bichromate of cerium. Small red transparent prisms, readily soluble in water.
- 12. Molybdate of cerium is easily obtained by double decom-It is a white powder insoluble in water, but soluble in several acids.¶
- 13. Oxalate of cerium. This salt may be obtained by adding oxalate of ammonia or oxalic acid to sulphate of cerium. When the oxalic acid is used, the salt falls like a piece of curd, which may be taken up on the end of a rod like so much soft resin. Whether allowed to remain in the liquid, or dried, it rapidly loses this property, and falls into a white powder. When heated it burns and leaves peroxide of cerium. It is insoluble in water and in oxalic acid. After being dried in as high a temperature as it could bear, without decomposition, its constituents were found by Dr. Steel to be

1 atom oxalic acid .	•	•	4.5
1 atom protoxide of cerium	•	•	<b>6·5</b>
			11**

- 14. Acetate of cerium. Acetic acid readily dissolves the protoxide of cerium, newly precipitated by means of alkalies. The solution, when saturated, has a sweet taste, and yields by evaporation small granulated crystals: readily soluble in water, but sparingly soluble in alcohol, and not altered by exposure to the air.++
- 15. Tartrate of cerium. When tartaric acid is digested upon recently precipitated protoxide of cerium, it forms a salt readily soluble in water, in consequence of the excess of acid which it contains. When the solution is mixed with a great quantity of water, white insoluble flakes of tartrate of cerium are precipitated. Tartaric acid occasions no precipitate in the sulphate, nitrate, or muriate of cerium; but tartrate of potash

<sup>†</sup> Berzelius. \* Hisinger and Berzelius. t Ibid. § Ibid. ¶ Ibid.

<sup>\*\*</sup> The quantity obtained in the analysis was 6.492 instead of 6.5.

<sup>++</sup> Hisinger and Berzelius, Gehlen's Jour. ii. 413.

Class L

- throws down the tartrate of cerium in the state of a white powder. It is soft, light, tasteless, and insoluble in water. It is soluble in nitric, muriatic, and sulphuric acids, and in pure alkalies.\*
- 16. Citrate of cerium. Muriate of cerium is not precipitated by citric acid. By digesting the acid on recently precipitated oxide, an insoluble compound is formed, which is rendered soluble by an excess of acid. The solution does not crystallize. Alcohol deprives it of its water and of part of its acid, but does not dissolve it.+
- 17. Succinate of cerium. When a few drops of succinate of ammonia are poured into muriate or nitrate of cerium, a precipitate is formed which soon disappears. When more of the re-agent is added, the succinate of cerium is separated in the state of a white powder. This salt is not wholly insoluble in water, as a small portion still remains in solution. Succinate of ammonia does not precipitate cerium from the acetate. This furnishes us with a ready means of separating iron from cerium when they happen to be mixed.
- 18. Benzoate of cerium. Benzoic acid occasions no precipitate in muriate of cerium; but when it is digested on recently precipitated oxide of cerium, a solution takes place. On cooling, the liquid first lets fall crystals of benzoic acid, then the benzoate of cerium falls in the state of a white insoluble powder.§

### SECT. XIII. - SALTS OF PEROXIDE OF CERIUM.

The salts of peroxide of cerium are distinguished by a yellow or orange colour. They have been very little examined; but it is probable that the characters (or at least most of them) given in the last section to the salts of protoxide of cerium will apply to them likewise.

- 1. Sesquisulphated peroxide of cerium. This salt may be obtained by dissolving peroxide of cerium in dilute sulphuric acid by a gentle heat. The orange-coloured solution obtained in this way, when cautiously evaporated, yields beautiful silky needles of a lemon yellow colour. When alcohol is added to the concentrated solution the salt falls down exactly like a piece of soft yellow resin, very adhesive, and which, by exposure to the air, becomes softer, but does not deliquesce. The
  - \* Hisinger and Berzelius, Vauquelin.
  - † Hisinger and Berzelius, Gehlen's Jour. ii. 113.
  - ‡ Ibid. ii. 414. § Ibid. ii. 413.

crystals are not altered by exposure to the air. When dis-sect. XIII. solved in a large quantity of water, a solution of sulphate of cerium is obtained, while a yellow insoluble disulphate of peroxide precipitates.

The salt reddens vegetable blues. When heated it melts into an orange-coloured liquid, which becomes yellow when all the water is driven off. A red heat decomposes it altogether. The constituents of this salt, according to the analysis of Dr. Steele, are

Sulphuric acid	•	•	7-491
Peroxide of cerium	•	•	7.072
Water	•	•	<b>5·438</b>
This is obviously equivalent to			
1; atom sulphuric acid 😁	•		7.5
1 atom peroxide of cerium	•	•	<b>7·0</b>
5 atoms water	•	•	5.625
			20.125

2. Disulphate of peroxide of cerium. This is the substance which precipitates when the preceding salt is dissolved in a great deal of water. It is a sulphur yellow, insoluble powder-Before ignition it is easily soluble in acids, but after being heated to redness it does not dissolve in nitric or muriatic acids or in aqua regia. 2.18 grains of this salt, analyzed by Dr. Steel, were found composed of

Sulphuric acid	•	•	. 5
Peroxide of cerium	•	•	14.4
This is obviously equivalent to			
1 atom sulphuric acid .	•	•	5
2 atoms peroxide of cerium	•	•	14
	<b>≠</b> r		19

- 3. Nitrate of peroxide of cerium. Peroxide of cerium dissolves with difficulty in nitric acid. The solution has a yellowish red colour.
- 4. Subsesquiphosphate of peroxide of cerium. This salt may be obtained by mixing together solutions of the nitrated peroxide of cerium and phosphate of soda. The precipitate, when washed and dried, is a light yellow powder composed, according to the analysis of Dr. Steel, of

Phosphoric acid	•	•	•	4.5
Peroxide of cerium		•		10.63

Class I. This is equivalent to

I atom phosphoric acid	, •	•	4.5
12 atom peroxide of cerium	•	•	10.5
_			
•			1.5

- 5. Selenite of peroxide of cerium. A lemon yellow powder, which lets go its acid when strong y heated.\*
- 6. Biselenite of peroxide of cerium. Obtained by dissolving the preceding salt in selenious acid. It is white, opaque and crystalline. It is soluble in water.+
- 7. Sesquioxalate of peroxide of cerium. This salt may be obtained exactly in the same way as the oxalate of cerium, only substituting the peroxide for the protoxide of cerium. The resinous-looking matter obtained is reddish yellow; but when dried it assumes the form of a white powder. Its constituents, according to the analysis of Dr. Steel, are

$1\frac{1}{2}$	atom	oxalic ac	id	•	•	•	6· <b>75</b>
1	atom	peroxide	of	cerium	•	•	7
1	atom	water	•	•	•	•	0.5625
							14.3125

### SECT. XIV .- SALTS OF ZIRCONIA.

Characters.

Zirconia dissolves in acids only when newly precipitated from its solutions and still moist. If it be dried, and especially if it be exposed to a red heat, it is acted on by acids with great difficulty.

- 2. The alkalies, the alkaline earths, and the earths proper, separate zirconia from all its combinations with acids.
- 3. The greater number of the salts of zirconia are insoluble in water. This is the case with the sulphate, sulphite, phosphate, fluate, borate, carbonate, selenite, oxalate, tartrate, citrate, mucate, and gallate. The muriate, nitrate, acetate, benzoate, and malate, are soluble in water.
- 4. The salts of zirconia have an astringent taste, harsh, and disagreeable, similar to some of the metalline salts.
- 5. When sulphuric acid is dropped into a salt of zirconia, a white precipitate falls.
- 6. When carbonate of ammonia is dropped into a salt of zirconia, a white precipitate appears, which is re-dissolved if an additional portion of the carbonate of ammonia be added.

- 7. Oxalate of ammonia and tartrate of potash occasion a sect. XIV. white precipitate when dropped into a salt of zirconia.
  - 8. Prussiate of potash throws down nitrate of zirconia white.
  - 9. Chromate of potash, a yellow precipitate.
- 10. The infusion of nut-galls, when dropped into a solution of zirconia, occasions a white precipitate. The hydrosulphuret of potash occasions no precipitate, if the solution be free from iron.
- 1. Sulphate of zirconia. This salt may be formed by dissolving zirconia or its hydrate in sulphuric acid, evaporating till the salt crystallizes, and freeing the crystals from all excess of acid, either by washing them in alcohol, or by exposing them for a quarter of an hour to a red heat. The dried salt dissolves slowly in cold, but rapidly in hot water. Ammonia throws down pure zirconia from the solution. Taste astringent. Its constituents, according to the analysis of Berzelius, are

Zirconia .	•	•		3·08
			. 100	— ••0ò*
This is obviously equivalent				<b>,</b>
1 atom sulphuric ac	:1a	•	•	3
l atom zirconia	•	•	•	3.75
				0.75

2. Disulphate of zirconia. This salt may be obtained by dissolving hydrate of zirconia in an aqueous solution of the preceding salt. When the solution is concentrated, we obtain first a gummy, and afterwards a white opaque matter, which is the salt in question. When heated, it swells like alum, giving out water, and when the temperature is raised to redness the acid also is disengaged. When we attempt to dissolve this salt in a great quantity of water it undergoes decomposition. Its constituents, according to the analysis of Berzelius, are

Sulphuric acid	•		39.73
Zirconia		•	60.27
This is obviously equivalen	t to		100 00†
1 atom sulphur			5
2 atoms zirconi		•	7.5
	•		

<sup>12.5</sup> 

Kong. Vet. Acad. Hand. 1824, p. 314.

3. Tris-sulphate of zirconia. This salt is obtained when the neutral sulphate is precipitated from its solution by alcohol. The precipitate is to be washed first with alcohol and then with water. It is a white, tasteless, insoluble white powder, composed, according to the analysis of Berzelius, of

Sulphuric acid	•	•	30.53
Zirconia .	•	•	69-47
			100.00*
iously equivalent to I atom sulphuric aci	id		5

This is obvi

3 atoms zirconia . 11.25 16.25

4. Nitrate of zirconia. This salt was first formed by Klaproth. Vauquelin has given us a detailed description of it. may be easily formed by pouring nitric acid on newly precipitated zirconia.

It always contains an excess of acid. By evaporating, a yellowish transparent matter is obtained, exceedingly tenacious and viscid, and which dries with difficulty. It has an astringent taste, and leaves on the tongue a viscid matter, owing to its being decomposed by the saliva. It is only very sparingly soluble in water; the greatest part remains under the form of gelatinous and transparent flakes. Like all the other salts into which zirconia enters, it is decomposed by heat. It is decomposed also by sulphuric acid, which occasions a white precipitate soluble in excess of acid; by carbonate of ammonia, which produces a precipitate soluble by adding more carbonate; and by an infusion of nut-galls in alcohol, which produces a white precipitate soluble in an excess of the infusion, unless the zirconia contains iron; in which case the precipitate is a gravish blue, and part of it remains insoluble, giving the liquor a blue colour. This liquor, mixed with carbonate of ammonia, produces a matter which appears purple by transmitted light, but violet by reflected light. Gallic acid also precipitates nitrate of zirconia of a grayish-blue, but the colour is not so fine. Most of the other vegetable acids decompose this salt, and form combinations insoluble in water.+

5. Carbonate of zirconia. This salt was formed by Vauquelin

<sup>\*</sup> Kong. Vet. Acad. Hand. 1824, p. 314.

<sup>†</sup> Vauquelin, Ann. de Chim. xxii. 199.

by precipitating zirconia from its solution in acids by alkaline 'Sect. XVI. carbonates. It is a tasteless white powder, composed of

44.5 acid and water 55.5 zirconia

#### 100.0

From the experiments of Klaproth, it would appear to contain but little carbonic acid, and therefore to be a sub-salt.

- 6. Phosphate of zirconia. A white powder, insoluble in water.
- 7. Borate of zirconia. A white insoluble powder.
- 8. Selenite of zirconia. A white powder, insoluble in water and in selenic acid. It is decomposed by heat.\*
- 9. Acetate of zirconia. This salt may be formed by pouring acetic acid on newly precipitated zirconia. It has an astringent taste. It does not crystallize, but when evaporated to dryness it forms a powder, which does not attract moisture from the air as acetate of alumina does.† It is very soluble in water and in alcohol. It is not so easily decomposed by heat as nitrate of zirconia, probably because it does not adhere so strongly to water.‡
- 10. Benzoate of zirconia. This salt is soluble in water, but its properties have not been investigated.
  - 11. Oxalate of zirconia. A white insoluble powder.
  - 12. Tartrate of zirconia. A white insoluble powder.
  - 13. Citrate of zirconia. A white insoluble powder.
  - 14. Mucate of zirconia. A white insoluble powder.
- 15. Malate of zirconia. This salt is soluble in water, but its properties have not been examined.
  - 16. Gallate of zirconia. A white insoluble powder.

#### SECTION XV. - SALTS OF THORINA.

The salts of thorina have not yet been examined in detail. I have given in the first volume of this work (p. 477) the few facts respecting them which have been ascertained by the researches of Berzelius. It will be sufficient to refer the reader to that place for the characteristic properties of thorina and its salts.

## SECTION XVI. - SALTS OF PROTOXIDE OF IRON.

The compounds which the acids form with the oxides of iron

- \* Berzelius, Ann. de Chim. et de Phys. x. 265.
- † Klaproth, Jour. de Phys. xxxvi. 188.
- 1 Vauquelin, Ann. de Chim. xxii. 206.

were formerly distinguished in chemistry by the epithet martial, because Mars was the title given by the alchymists to iron. The most important of these salts have been long known. Few metals attract oxygen and combine with acids with more facility than iron; many of its salts, therefore, are found ready formed, or at least are often formed during the multiplicity of operations to which this very useful metal is exposed. Some of these salts have been long of great importance in manufactures. They form the basis of writing ink and of the black dye, and are employed also to communicate several other colours to cloth.

The protosalts of iron may be distinguished by the following properties.

Characters.

- 1. The greater number are soluble in water; and in general the solution has a greenish or yellowish red colour, and an astringent taste.
- 2. Prussiate of potash occasions in these solutions a precipitate of a deep blue, or at least which acquires that colour on exposure to the atmosphere, being sometimes white.
  - 3. Hydrosulphuret of potash occasions a black precipitate.
- 4. Sulphuretted hydrogen renders the solution nearly colourless, but occasions no precipitate.
- 5. Gallic acid, or the infusion of nut-galls, occasions a black or purple precipitate, at least if the solution has been for some time exposed to the air.
- 6. Phosphate of soda, when dropped into a salt of iron, occasions a white precipitate.
- 7. Benzoate of ammonia does not precipitate the protosalts of iron, but if they be heated with nitric acid, and then neutralized, it throws them down yellow.
- 8. The action of succinate of ammonia on the salts of iron is similar to that of benzoate.
- 1. Sulphate of iron. Concentrated sulphuric acid acts but very slowly upon iron, unless it be assisted by heat. In that case the metal is oxidized, and sulphurous acid gas exhaled. But diluted sulphuric acid dissolves iron with great rapidity, and abundance of hydrogen gas is emitted. In this case the water is decomposed, its oxygen combines with the iron, while its hydrogen is emitted. The solution has a green colour, and when evaporated immediately, yields crystals of sulphate of iron, but if allowed to remain exposed to the atmosphere, it gradually attracts more oxygen, and is converted into persulphate, unless it contains an excess of acid, which retards, and, when sufficiently abundant, prevents the change.

This salt was known to the ancients, and is mentioned by Sect. XVI. Pliny under the names of misy, sory, and calchantum.\* In History. commerce it is usually denominated green vitriol or copperas. It is not prepared by dissolving iron in sulphuric acid, but by moistening the pyrites which are found native in abundance, and exposing them to the open air. They are slowly covered with a crust of sulphate of iron, which is dissolved in water, and afterwards obtained in crystals by evaporation. Sometimes the salt is found ready formed, either in a state of solution in water or mixed with decayed pyrites. In some cases it is found necessary to roast the pyrites before they can be made to undergo spontaneous decomposition. This is most probably owing to the compact state of the pyrites in those cases, and the absence of all uncombined iron. Pyrites is in fact a bisulphuret of iron. The roasting reduces it to the state of sulphuret, which decomposes very readily. The solution always contains an excess of acid. Hence it is necessary, in order to obtain the salts in crystals, to throw into it a quantity of old iron.

Sulphate of iron has a fine green colour. Its crystals are Properties. oblique rhombic prisms, as was first shown by Dr. Wollaston. The base of the prism is inclined to either of the lateral faces at an angle of 99° 20′. The inclination of the lateral faces to each other is 82° 20′. The angles of the prism are frequently replaced by one or two faces.† It has a strong styptic taste, and always reddens vegetable blues. Its specific gravity is 1.980. The following table exhibits the solubility of 1 part of this salt in water at different temperatures, as determined by Brandes and Firnhaber:

Temperature 50° 59° 75°  $91^{\circ}_{\frac{1}{2}}$  115° 140° 183° 194° 212° Water 1.64 1.43 0.87 0.66 0.44 0.38 0.37 0.27 0.30 The solution is light green. Alcohol and sulphuric acid throw down from it the anhydrous salt. When exposed to the air, its surface gradually becomes opaque, and is covered with a yellow powder, because it absorbs oxygen, and is partially converted into persulphate. This change takes place much more rapidly and completely if the salt be moistened with water. The cause of these phenomena was first explained by Scheele.

When heated it melts, gradually loses its water of crystallization, and by a strong heat sulphuric acid is driven off, and there remains behind a red powder, formerly known by the name of colcothar of vitriol, which is either a mixture of red

<sup>\*</sup> Lib. xxxiv. c. 12.

<sup>+</sup> Brooke, Annals of Philosophy (2d series), vi. 120.

oxide of iron and persulphate, or pure oxide, according to the heat applied. When this salt is distilled, there comes over first water slightly acidulated with sulphuric acid, and afterwards a very strong fuming acid, formerly known by the name of glacial oil of vitriol. The residuum is the same mixture of oxide and persulphate which is obtained by calcination in the open air. This decomposition, which sulphate of iron undergoes when heated, enables it in many cases, in a high temperature to act nearly the same part as sulphuric acid. Hence it is often employed by manufacturers to disengage the weaker acids from their bases.

When the crystals of sulphate of iron are moderately heated, they assume at first a white colour; the same change of colour is observed when the salt, in the state of powder, is infused in alcohol. Hence we see the separation of the water changes the colour from green to white, and if water be now poured on the white powder, it becomes again green.

The sulphate of iron is decomposed by the alkaline phosphates and borates, and by the greater number of those salts whose base forms an insoluble compound with the sulphuric acid, as nitrate of silver, of lead, of barytes, &c.

Its constituents are

1 atom sulphuric acid	•	•	5
1 atom protoxide of iron		•	4.5
7 atoms water .	•	•	7.875
			17.375

- 2. Bisulphate of iron. Sulphuric acid dissolves crystallized or anhydrous sulphate of iron, assuming at first a rose red, but when fully saturated acquiring a purple red colour. When water is gradually added to the solution, so as to dilute it without any increase of temperature, the colour becomes gradually more dilute, and at last disappears. It vanishes also when the solution is heated, while, at the same time, sulphurous acid is exhaled, and sesquisulphate of peroxide is precipitated.\*
- 3. Sulphite of iron. This salt can only be formed by dissolving recently precipitated protoxide of iron in sulphurous acid. It is insoluble in alcohol, and when exposed to the air is converted into sulphate of iron.
- 4. Subsulphite of iron. Sulphurous acid attacks iron with rapidity, much heat is produced, and the solution assumes at

<sup>\*</sup> Bussy and Lecanu, Jour. de Pharmacic, xi. 341.

first a brown colour, which gradually passes into a green. During seet. XVL this solution no hydrogen gas is emitted except a few hubbles at first. The iron is oxidized at the expense of the acid, half the oxygen of which combines with the iron, and converts it into black oxide, while the whole sulphur and the remaining oxygen unite with the iron. The salt, therefore, which is obtained by this process, is not sulphite of iron, but subsulphite. These phenomena were first described by Berthollet.\* When sulphuric acid or muriatic acid is poured into this solution, sulphurous acid is disengaged with effervescence, and if these acids be added in sufficient quantity, a portion of sulphur is precipitated.

When the solution is exposed to the air, crystals of hyposulphite of iron are formed, and at the same time a red powder is deposited, probably consisting of perhyposulphite of iron with excess of base. The crystals dissolved in water and exposed to the air are gradually converted into sulphate of iron.+

- 5. Hyposulphite of iron. Mr. Herschell has ascertained that this salt is formed when carbonate of iron is dissolved in sulphurous acid, and the liquid boiled over flowers of sulphur. Its taste is strongly ferruginous. It does not crystallize, but yields a glutinous mass of a dirty white colour not unlike glazier's putty.‡
- 6. Hyposulphate of iron. This salt is obtained when hyposulphate of barytes and sulphate of iron are mixed in the requisite proportions. The filtered liquid is to be exposed in a warm place to spontaneous evaporation. Crystals are obtained in oblique rhombic prisms, having the colour and taste of sulphate of iron. When exposed to the air they become brown on the surface, but undergo no farther alteration. readily in water, but not in alcohol. Its constituents, according to the analysis of Heeren, are

1 atom hyposulphuric acid 1 atom protoxide of iron. 4.5 5 atoms water 5.625

19.1258

7. Nitrate of iron. This salt was first formed by Davy. It may be obtained by dissolving iron in dilute nitric acid till it refuses to take up any more, taking care that the temperature of the liquid does not become elevated. The solution is at

<sup>\*</sup> Ann. de Chim. ii. 58.

<sup>+</sup> Fourcroy, vi. 200.

<sup>\*</sup> Ann. de Chim. ii. 58. † Fourcroy, vi. 200. ‡ Edin. Philos. Jour. i. 22. § Poggendorf's Annalen, vii. 181.

first brown and opaque, owing to the deutoxide of azote with which it is impregnated, but it gradually assumes a green colour, with a slight shade of yellow. It may be concentrated in the vacuum of an air-pump over sulphuric acid. It deposites pretty regular crystals of nitrate of iron. They are oblique rhombic prisms, transparent, and have a light green colour. These crystals redden vegetable blues, their taste is sweet and astringent. They dissolve readily in water. When heated they melt, water and nitric acid are evolved, and the iron peroxidized. The constituents of this salt, by my analysis, are

1	atom nitric acid .		6.75
1	atom protoxide of iron	•	4.5
$7\frac{1}{2}$	atoms water	•	8.4375

19.6875

This salt cannot be preserved, the iron is gradually peroxidized, and the crystals deliquesce.

- 8. Chlorate of iron. As far as we know at present this salt does not exist. Chloric acid dissolves iron with great rapidity without the evolution of any gas. The iron very speedily passes to the red oxide at the expense of the chloric acid which it decomposes. When a current of chlorine gas is passed through water, having the red oxide of iron diffused through it, the oxide is dissolved, but the compound formed appears to be merely a compound of chlorine and red oxide of iron, or a chloride of the red oxide.\*
- 9. Carbonate of iron. Liquid carbonic acid, when kept in contact with iron, attacks it slowly, and dissolves a sufficient quantity of it to acquire a sensibly chalybeate taste. When exposed to the air, the iron is gradually precipitated in the state of oxide, and by boiling it is deposited in the form of a yellow ochre, still retaining a portion of acid. This carbonate often exists native in mineral waters. It may be obtained also by precipitating the sulphate of iron by means of an alkaline carbonate. In that case it is always in the form of a green mass, or hydrate, which gradually becomes black if the contact of air be excluded.

This salt exists native in great abundance, though rarely in a state of purity. What is called *iron-stone*, or *clay iron* stone, from which almost all the immense quantity of iron manufactured in this country is smelted, and which occurs in beds and

detached masses in the coal formation, is nothing else than a sect. XVI. carbonate of iron intermixed with more or less clay, coal, and sometimes limestone. The pure carbonate of iron occurs occasionally crystallized in mineral veins. It is found in Cornwall, accompanying copper ore, and in the county of Durham accompanying galena. It is often in crystals, and the shape of the crystals approaches very near to that of calcareous spar, an obtuse rhomboid; in which the continuous faces at the summit make angles of 107° instead of 105° 5', which is their inclination in calcareous spar. The crystals are sometimes octahedrons, and sometimes six-sided prisms. The colour is often white, with a shade of yellow or brown, and sometimes almost black. Its specific gravity is about 3.8. Its constituents, when pure, are

1 atom carbonic acid		•	2.75
1 atom protoxide of iron	•	•	4.5
			7.25

But it often contains a little carbonate of lime, carbonate of manganese, or carbonate of magnesia; and it occurs united with one or more of these salts in chemical combination. tutes an excellent medicine. But the carbonate of iron of the Pharmacopœia contains very little true carbonate. It is chiefly a hydrated peroxide of iron; not possessed of nearly so much efficacy as the carbonate does.

10. Phosphate of iron. Phosphoric acid has but little action upon iron. However, if that metal remain exposed to the contact of phosphoric acid, or even to the solutions of salts which contain that acid, it is gradually oxidized, and converted into phosphate of iron. When phosphate of soda is mixed with sulphate of iron, a white precipitate falls which is bulky, and consists of phosphate of iron. It speedily becomes gray, and when washed with water it becomes greenish-blue, owing obviously to the gradual peroxidizement of the iron. So that the artificial phosphate of iron can scarcely be rendered fit for examination. But from the phenomena connected with its precipitation, there is reason to conclude that it is a neutral phosphate composed of

1 atom phosphoric acid 1 atom protoxide of iron 4.5

Class I.	native, and have been subjected to			
	(1.) Hydrated phosphate of iron	comp	osed o	f
•	I atom phosphate of iron	•	•	9
	3 atoms water	•	•	3.375
				12.375
	(2.) Hydrated subsesquiphosphat	te con	nposed	of
	1 atom phosphoric acid	•	•	4.5
	$1\frac{1}{2}$ atom protoxide of iron	_		6.75
	$2^{\frac{1}{2}}$ atoms water	•	•	2.8125
				14.0625
	(3.) Hydrated diphosphate of iro	n con	posed	of
	1 atom phosphoric acid	•	•	4.5
	2 atoms protoxide of iron			9
	4 atoms water	•	•	4.5
				<del></del> 18·0
	11. Arseniate of iron. When a	reani	ata of	-
	into a solution of sulphate of iron			
	which is arseniate of iron. It is taste			
	but easily soluble in nitric and mur			
	subjected to analysis; but there are		_	
	of iron, which occur native exactly			
	to the analogous phosphates of iron	. Tl	iese ar	·e
Native arse- niates.	(1.) Hydrous arseniate, composed	d of		
	1 atom arsenic acid	•	•	7.25
	1 atom protoxide of iron	•	•	4.5
	2 atoms water	•	•	2.25
				14
	(2.) Hydrous subsesquiarseniate	comp	osed o	
	l atom arsenic acid	comp	oscie o	7.25
		•	•.	6·75
	$1\frac{1}{2}$ atom protoxide of iron	•	•	
	3 atoms water	•	•	3·375 
				17:375
	(3.) Hydrous diarseniate compos	ed of		
	1 atom arsenic acid	•	•	7.25
	2 atoms protoxide of iron	•		9
	6 atoms water	•	•	6.75

Native silacates.

12. Borate of iron. Boracic acid acts very feebly upon iron:
but borate of iron may be obtained very readily by pouring liquid borate of soda into a solution of sulphate of iron. A pale yellow powder immediately precipitates, which is the salt required. This salt is insoluble in water. Before the blowpipe it melts readily into a globule of glass.\*

13. Silicate of iron. The brown coloured hard slag from the smelting of copper ore, is either a silicate or bisilicate of iron, according to circumstances. There occur native no fewer than six species of silicated iron minerals. I merely give the names of these minerals in this place, reserving the description of them for a subsequent work which I intend to publish on

mineralogy and geology.

(1) Hydrous disilicate compos	ed of	•	
1 atom silica		•	<b>2</b>
2 atoms protoxide of iron		•	9.0
l atom water	•	•	1.125
			12.125
(2.) Chamoisite or bihydrated	disili	cate c	omposed o
1 atom silica		•	<b>2</b>
2 atoms protoxide of iron	•	•	9
2 atoms water	•	•	$2 \cdot 25$
			13.25
(3.) Anhydrous silicate compo	sed o	$\mathbf{f}$	
1 atom silica		•	$oldsymbol{2}$ .
1 atom protoxide of iron	•	•	4.5
			6.5
4.) Hydrous silicate compose	d of		•
l atom silica		_	2
1 atom protoxide of iron	_		4.5
l atom water	•	•	1.125
			7.625
5.) Hedenbergite or bihydrat	ed te	rsilica	
3 atoms silica			6
1 atom protoxide of iron	•	-	4.5
2 atoms water	•	•	2.25

<sup>\*</sup> Scheele, Crell's Annals, i. 114. Eng. Trans.

12.75

(6.) C	hloropal composed of			
3	atoms silica	•	•	6
1	atom protoxide of iron	•	•	4.5
21	atoms water	•	•	2.8125
				19.9105

14. Selenite of iron. Selenious acid scarcely dissolves iron; but the salt may be formed by mixing solutions of a protosalt of iron and an alkaline selenite. It precipitates in the form of a white matter which gradually becomes yellow as the air acts upon it. When muriatic acid is poured on it, and heat applied, the acid is decomposed and selenium disengaged.

15. Biselenite of iron is formed when the preceding salt is dissolved in selenious acid, or when a protosalt of iron is mixed with an alkaline biselenite. It is but little soluble and gradually falls down. When a solution containing it is heated, this salt is decomposed, and a brown precipitate falls.

- 16. Antimoniate of iron. Antimoniate of potash precipitates iron perfectly white, and the antimoniate of iron preserves its white colour as long as it is under water. But when dried in the open air it becomes yellowish-gray. When heated it gives out water and becomes red. Before the blow-pipe on charcoal it is reduced, the antimony is volatilized, and the iron remains obedient to the magnet.\*
- 17. Chromate of iron. This salt does not exist. The protoxide of iron has the property of absorbing oxygen from chromic acid, and of being converted into peroxide, while the chromic acid is reduced to the state of green oxide.
- 18. Titaniate of iron. Though we are not acquainted with any good method of combining titanic acid with protoxide of iron, yet several combinations occur native, which must be considered as titaniated salts of iron. Of these I shall merely give the names in this place.

ve the names in this place.			
(1.) Menachanite or titaniate of	iron,	comp	osed of
1 atom titanic acid	•	•	5.25
1 atom protoxide of iron	•		4.5
			9.75
(2.) Nigrin or quatertitaniate of	iron	aamn	
· , • -	11011,	comp	oseu oi
4 atoms titanic acid	•	•	21
l atom protoxide of iron			4.5

<sup>\*</sup> Berzelius, Nicholson's Journal, xxxv. 42.

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(3.) Iserine or tetratitaniate of ire	on, co	mpos	ed of
l atom titanic acid		•	5.25
4 atoms protoxide of iron	•	•	18
•			23.25
(4.) Titaniferous iron ore compos	ed of	•	
l atom titanic acid	•	•	5.25
8 atoms protoxide of iron	•	•	36.
			41.25

19. Columbate of iron. It appears from the analysis of Berzelius that the tantalite of Kimïto, if we abstract a little lime, manganese, silica, and tin, is composed of one atom of columbic acid united to an atom of protoxide of iron.

20. Oxalate of iron. This salt may be obtained by pouring oxalic acid or oxalate of ammonia into a solution of sulphate of iron. It instantly falls in the state of a beautiful yellow powder. When heated moderately on the sand-bath it gives out water and becomes brown. Soon after it catches fire and burns like tinder. Its constituents, by my analysis, are

1	atom	oxalic a	cid	•	•	4.5
1	atom	protoxid	e of i	iron		4.5
2	atoms	water	•	•	•	2.25
						11.25

21. Acetate of iron. This salt was first described by Davy. It may be formed by dissolving iron or its sulphuret in acetic acid. The solution is light green and transparent, and crystallizes in prisms. When we attempt to filter the solution it absorbs oxygen with great rapidity and becomes black and opaque. When concentrated in the vacuum of an air-pump over sulphuric acid, it is obtained in a fibrous state and of a very light green colour, almost white. Its taste is sweet, astringent and acid, and it reddens vegetable blues. It dissolves readily in water, and the solution becomes immediately dark-coloured. The constituents of this salt, according to my analysis, are:

1 atom acetic acid	•	•	6.28
1 atom protoxide of ire	on	•	4.5
3 atoms water .	•	•	3·3 <b>75</b>

Doubtless the crystals contain more water than the fibrous salt, which alone I subjected to analysis.

- 22. Lactate of iron. Lactic acid dissolves iron with rapidity when assisted by heat. The solution, when left to itself, lets fall a great number of small crystals in the shape of fine four-sided needles. This salt is not altered by exposure to the air. It is scarcely soluble in water, and contains hardly any water of crystallization. When held to the flame of a candle it does not melt, but burns with flame, and leaves peroxide of iron. Its colour is at first white; but when two or three times dissolved in water it is divided into two subspecies; the first, which has a brown colour, is soluble in water and crystallizes with difficulty. The other, which contains an excess of oxide, is white.\*
- 23. Formate of iron. Formic acid dissolves the hydrated protoxide of iron. The solution is colourless, but soon becomes covered with a crust having the metallic lustre. When heated protoxide of iron is precipitated, and formic acid remains in solution. It would appear from this that the salt cannot be procured in a solid state.+
- 24. Tartrate of iron. This salt is easily obtained by mixing rather concentrated solutions of sulphate of iron and tartrate of potash in the atomic proportions. In 24 hours, the tartrate of iron will be found encrusting the bottom and sides of the dish. It is in transparent but very irregular crystals. They are solid, not altered by exposure to the air, and having an inky but weak taste. Its constituents, by my analysis, are as follows:

1 atom tartaric acid . . . 8.251 atom protoxide of iron . . 4.52 atoms water . . . 2.25

15

- 25. Vinate of iron. This acid dissolves iron with the evolution of hydrogen gas, and when the solution is concentrated it deposites small white needles, soluble with difficulty in water and which speedily absorb oxygen from the atmosphere. ‡
- 26. Citrate of iron. This salt may be obtained by dissolving iron filings in a solution of citric acid till the acid is saturated, taking care that air is excluded from the liquid during the solution. The solution is nearly colourless and deposites a white powder on standing, which is citrate of iron. It has an astrin-

<sup>\*</sup> Braconnot, Ann. de Chim. lxxxvi. 94. + Göbel. + Walchner.

gent and sweet taste; dissolves readily in water; but is inso- sect. XVI. luble in alcohol. When exposed to the air it speedily attracts oxygen, and becomes first yellow and then olive-green, being converted into percitrate.

27. Malate of iron. Malic acid forms with iron a brown solution, which does not yield crystals.\*

- 28. Mucate of iron. Mucic acid does not precipitate iron from sulphuric acid.+
- 29. Pyromucate of iron. Pyromucic acid dissolves iron with the evolution of hydrogen gas and a salt is formed which dissolves readily in water. ‡
- 30. Succinate of iron. Succinic acid dissolves the protoxide of iron, and yields by evaporation small brown transparent radiated crystals.§
- 31. Benzoate of iron. Yellowish crystals efflorescing in the air and soluble in water and alcohol. Benzoate of ammonia does not precipitate the protoxide of iron.
- 32. Gallate of iron. Mr. Proust first observed, that the gallic acid does not occasion any precipitate when poured into salts of iron containing that metal in the state of protoxide. Hence it follows that the gallate of iron, if it be formed in these cases, is very soluble in water and without colour.
- 33. Boletate of iron. Boletic acid dissolves iron with the evolution of hydrogen gas, and the solution has a yellow colour. The salt has not yet been obtained in a solid state.
- 34. Suberate of iron. Suberic acid and suberate of ammonia precipitate sulphate of iron white. The precipitate when heated melts, and by increasing the temperature the salt is destroyed.
- 35. Pinate of iron. This salt at the temperature of boiling water is in the state of a powder. It is colourless at first; but by exposure to the air becomes dark brown, owing to the absorption of oxygen. ¶
- 36. Silvate of iron is insoluble in alcohol, but dissolves in ether, and when the solution is exposed to the air it speedily becomes brown by the absorption of oxygen.\*\*
- 37. Sulphovinate of iron. Sulphovinic acid dissolves iron with the evolution of hydrogen gas. The solution is colourless, has a sweet taste, and is not precipitated by chloride of barium.

<sup>\*</sup> Scheele, Crell's Annals, ii. 10. Eng. Trans. † Scheele, ii. 80.

<sup>‡</sup> Labillardiere. § Wenzel's Verwandtschaft, p. 240. Grindel's Edit.

<sup>|</sup> Brandes, Schweigger's Jour. xxxiii. 102.

<sup>¶</sup> Unverdorben, Poggendorf's Annalen, xi. 236.

<sup>\*\*</sup> Unverdorben, ibid. p. 401.

By evaporation we obtain yellow-coloured four-sided prisms, which are very soluble in water and in alcohol. When these crystals are exposed to the air they effloresce, and in a few days become opaque.\*

38. Sulphonaphthalate of iron. Iron dissolves in sulphonaphthalic acid with the evolution of hydrogen gas. Protoxide of iron, while still moist, dissolves in the acid and forms a neutral solution capable of crystallizing. By exposure to the air it slowly acquires oxygen.

## SECTION XVII. - SALTS OF PEROXIDE OF IRON.

#### Characters.

The aqueous solution of these salts has usually a reddish or yellowish colour. They have a sweetish, astringent, and very harsh taste. The greater number of them are incapable of crystallizing. In general they are soluble in alcohol. They are precipitated of a very dark blue, almost black, by prussiate of potash. Their other characters correspond with those given to the protosalts of iron.

1. Sesquisulphated peroxide of iron. When sulphate of iron is peroxidized by means of nitric acid and cautiously concentrated till the whole nitric acid is driven off we obtain a red coloured matter, which dissolves only partially in water. The dissolved portion has a red colour with a tint of yellow,—the taste is astringent and very harsh. When evaporated to dryness it speedily absorbs moisture and deliquesces into a liquid. Alcohol dissolves it readily. It strongly reddens vegetable blues. When strongly heated so as to drive off all the water it becomes white. Its constituents, by my analysis, (abstracting the water) are:

$1\frac{1}{2}$ 2	atom	sulphuric a	ıcid	•	•	7.5
1 :	atom	peroxide o	f iron	•	•	5
						12.5

2. Tetrasulphated peroxide of iron. The insoluble portion remaining after the sulphate of iron, treated as described while giving an account of the formation of the last salt, has been washed in water, is a red-coloured powder, destitute of taste, and insoluble in water. When heated to redness, it gives out water, and assumes a brownish-red colour. By a stronger heat, the sulphuric acid is driven off. When the sesquisulphated peroxide of iron is mixed with ammonia in too

<sup>\*</sup> Vogel, Gilbert's Annalen, lxiii. 96.

<sup>†</sup> Faraday, Annals of Philosophy (2d series), xii. 210.

small a proportion to decompose it completely, the same inso- sect. XVII. luble salt is thrown down. The constituents of it, when dried in the open air, are, according to the analysis of Berzelius,

1 atom sulphuric acid	•	5
4 atoms peroxide of iron	•	20
6 atoms water	•	6.75
		31.75

3. Sesquinitrated peroxide of iron. This salt was first formed by Vauquelin, who obtained it by leaving nitric acid long in contact with black oxide of iron. It crystallizes, and the crystals form spontaneously when a bar of iron is placed into a glass containing moderately strong nitric acid, so as to be only partly under the surface of the acid. I have obtained crystals in this way, partly in flat, colourless rhomboids, and partly in four-sided prisms, with square bases. The prisms are sometimes six and sometimes eight-sided, from two or all the lateral edges of the prisms being replaced by tangent planes. The taste is astringent and acid, and the salt powerfully reddens vegetable blues. The crystals deliquesce rapidly when exposed to the air, into a reddish-brown liquid. When heated, they fuse into a deep, yellowish-red coloured liquid. The constituents of these crystals, by my analysis, are

$1\frac{1}{2}$	atom nitric acid	d	•	10.125
1	atom peroxide	of iron	1	5
8	atoms water	•	•	9
			,	

24.125

4. Octakinitrate of peroxide of iron. When nitric acid is digested over hydrated peroxide of iron, till it refuse to dissolve any more, and afterwards diluted and raised to the boiling temperature, a brown, tasteless powder falls, which constitutes an octakinitrated peroxide. It is slightly soluble, according to Berzelius, in pure water. Its constituents, according to the analysis of Grouvelle, are as follows:

1 atom nitric acid .		6.75
8 atoms peroxide of iron	n.	40
2 atoms water	•	2.25

49\*

5. Phosphated peroxide of iron. When a saturated solution

<sup>\*</sup> Ann. de Chim. et de Phys. xix. 138.

of peroxide of iron is mixed with a solution of phosphate of soda in sufficient quantity, and after being diluted with a great deal of water, ammonia is poured into the liquid, the phosphated peroxide falls in the form of a white powder, tasteless, and scarcely soluble in water, but slightly soluble in nitric or muriatic acid. It requires 1500 times its weight of water to dissolve it. It is said also to be soluble in an aqueous solution of ammonia. It is obvious from the experiments of Berthier, that the constituents of this salt are

1 atom phosphoric acid . 4.5
1 atom peroxide of iron . 5
9.5\*

My experiments lead to the conclusion, that when dried in the open air, it contains  $7\frac{1}{6}$  atoms water.

6. Diphosphated peroxide of iron. When the preceding salt is digested in caustic potash ley, it assumes a deep, brownish-red colour. The new salt thus formed is tasteless, and insoluble in water. When heated to redness, the colour becomes almost black. I found the constituents of the red salt dried in the open air

I am disposed from this to conclude, that the true constitution of the salt is

1 atom phosphoric acid . 4.5
2 atoms peroxide of iron . 10
3 atoms water . . 3.375

- 7. Arseniated peroxide of iron. This salt may be formed by oxidizing the neutral arseniate of iron, by boiling it in nitric acid. It is then to be evaporated to dryness, or precipitated by ammonia. It is not soluble in a solution of ammonia.
- 8. Sesquarseniated peroxide of iron. The sesquichloride of iron gives with arseniate of soda a white precipitate. When heated, it loses its water, and becomes red. When heated to redness, it phosphoresces a little, and becomes yellow. It may be obtained also by mixing nitrated peroxide of iron with an excess of arseniate of soda. When dry, it has a buff colour,

with a conchoidal fracture. When pounded, it has a fine orange colour. Tasteless, reddens vegetable blues. Dissolves readily in strong muriatic acid, and the solution is red. Dissolves also in nitric and sulphuric acid. Its constituents, from the analysis of Chenevix \* and Berzelius, would appear to be

 $1\frac{1}{2}$  atom arsenic acid . 10.875 1 atom peroxide of iron 5 3 atoms water . . 3.375

9. Subarseniated peroxide of iron. When either of the two preceding salts is treated with an excess of potash, it is converted into a brown-coloured matter, like hydrated peroxide of iron. It is insoluble in ammonia, and though boiled with potash, loses no more acid. Its constituents, according to the analysis of Berzelius, are as follows:

l atom arsenic ac	id	•	<b>7·25</b>
16 atoms peroxide	of ir	on	80.00
12 atoms water	•	•	13.50

## 100.75

- 10. Borated peroxide of iron. A yellowish powder, not soluble in water. When heated, it becomes brown, and finally melts into a glass.
- 11. Bisilicated peroxide of iron. Davy observed, that the ochre deposited from the mineral water at Lucca, is a compound of 4 parts by weight of peroxide of iron, and three parts of silica. This is nearly

2 atoms silica	•	•	4
l atom peroxide	•	•	5
			•

I found a similar compound of silica and peroxide of iron in some of the Leamington mineral waters, but only in small quantity.

It would not be surprising if some of the yellow ochres should prove similar compounds of silica and peroxide of iron.

12. Sesquiselenited peroxide of iron is easily obtained by dropping an alkaline selenite into a persalt of iron. It is a white powder, which becomes yellowish on being dried. When

<sup>\*</sup> Phil. Trans. 1801, p. 225.

<sup>†</sup> When dried simply by exposure to the atmosphere, I found in it 5 atoms of water.

- heated it gives out its water and becomes red, and at a high temperature the acid may likewise be disengaged.
  - 13. Biselenited peroxide of iron. When iron is dissolved in a mixture of selenious acid and nitro-muriatic acid at the boiling temperature, taking care that the whole of the nitric acid is not decomposed, the liquid deposites during its cooling a salt of a pistachio green colour on the sides of the vessel. This salt, which is insoluble in water, Berzelius considers as a biselenited peroxide of iron.
  - 14. Subselenited peroxide of iron. When either of the two preceding salts is digested in ammonia, a portion of the acid is separated, and a subselenite formed, which passes through the filter, and which may be deprived of its acid by the action of heat.\* According to Berzelius, it is composed of about

\_\_\_\_

13.66

- 15. Antimoniated peroxide of iron. A light yellow, insoluble powder.
- 16. Pentachromated peroxide of iron. When neutral solutions of peroxide of iron in muriatic acid and chromate of potash are mixed, a dark reddish-brown precipitate falls in large flocks. When this matter is washed and ignited, it has a brown colour, with a shade of red, is tasteless, and insoluble in water. Its constituents, by my analysis, are

17. Dichromated peroxide of iron. When the liquid from which the preceding salt fell is cautiously evaporated to dryness, and the residue mixed with water, an orange-coloured powder remains, which is slightly soluble in water. When this matter is dried in the open air, without the application of heat, its constituents, by my analysis, are

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 337.

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1 atom chromic acid 6.5

2 atoms peroxide of iron. 10

5 atoms water 5.625

22.125\*

18. Molybdated peroxide of iron. A brown powder. †

19. Oxalated peroxide of iron may be obtained by dissolving red oxide of iron in oxalic acid. It has the form of a yellow powder, scarcely soluble in water, and incapable of crystallizing.t It is slightly soluble in oxalic acid.

20. Acetated peroxide of iron may be obtained either by dissolving hydrated peroxide of iron in acetic acid, or by mixing together solutions of acetate of lead and sulphated peroxide in the requisite proportions. A red-brown, opaque liquid is obtained (almost black), having an inky taste, reddening vegetable blues, and incapable of yielding crystals, but assuming the appearance of a jelly when sufficiently concentrated.

There exists also a diacetated peroxide of iron, in the state of a yellow powder, insoluble in water.

- 21. Lactated peroxide of iron. A brown salt, not crystallizable, but readily dissolving in water.§
- 22. Formated peroxide of iron. The hydrated peroxide of iron dissolves very slowly in formic acid. The brownish-yellow solution, when sufficiently concentrated, deposites small, soft, reddish-yellow needles, easily soluble in water, but with difficulty in alcohol.
- 23. Mellated peroxide of iron. Mellitic acid, when dropt into nitrated peroxide of iron, throws down an isabella yellow powder, soluble in muriatic acid.
- 24. Tartrated peroxide of iron. A gelatinous, not crystallizable, but very soluble salt. When alkalies are dropt into the solution of this salt, they do not precipitate the oxide of iron, but merely a ditartrated peroxide.
- 25. Vinated peroxide of iron. Vinic acid dissolves hydrated peroxide of iron, and assumes a brownish-yellow colour. This solution gradually loses its colour by keeping, the iron being converted into protoxide. \*\*
- 26. Pyrotartrated peroxide of iron. The alkaline pyrotartrates throw down the peroxide of iron from its solutions, like the succinates or benzoates.

† Scheele.

<sup>\*</sup> Phil. Trans. 1827, p. 218.

<sup>‡</sup> Bergman, i. 268. | Arfvedson, Margrauff.

<sup>§</sup> Scheele and Braconnot.

<sup>¶</sup> Klaproth.

<sup>\*\*</sup> Walchner.

- 27. Citrated peroxide of iron. Dark-brown, brittle while cold, but becoming plastic when heated, easily soluble in water. According to M. H. Rose, the solution of this salt is not precipitated by alkalies.
- 28. Malated peroxide of iron. A brown, gum-like mass, not altered by exposure to the air, easily soluble in water, and alcohol. This salt is not precipitated by the alkalies.\*

  29. Pyromucated peroxide of iron. A lemon-yellow powder.
- 30. Succinated peroxide of iron. Succinate of potash or of ammonia precipitates peroxide of iron from its neutral solutions, in light brownish-red flocks, which become darker coloured when dried. This salt is not soluble in cold water; but when boiled in water, it is decomposed into bisuccinate, which dissolves, and disuccinate, which remains in the state of an insoluble powder. From the analysis of Bucholz, this salt, when simply dried in the open air, would seem to be a compound of

1	atom	succinic a	acid	•	6.25
1	atom	peroxide	of iro	n	5.00
$1\frac{1}{2}$	atom	water	•	•	1.6878

## 12.9375†

- 31. Bisuccinated peroxide of iron. Obtained by boiling the preceding salt in water. The solution is not precipitated by alkalies. When concentrated by evaporation, it deposites translucent plates.±
- 32. Subsuccinated peroxide of iron. The powder which remains undissolved when succinated peroxide of iron is boiled in water. It contains very little acid; but has not yet been accurately analyzed.

It was M. Rose, senior, that first pointed out the method of separating peroxide of iron from manganese, by means of an alkaline succinate.

33. Benzoated peroxide of iron. Benzoate of ammonia completely precipitates a neutral persalt of iron. The precipitate is flesh red. When heated, it melts into a reddish-yellow, fatty mass, the acid is destroyed, and protoxide of iron remains. When the salt is digested in aqueous potash or ammonia, the salt is partially decomposed, and a reddish-coloured solution is obtained. The salt is also decomposed into super and sub-

t Wenzel. + Gehlen's Jour. ii. 518.

<sup>§</sup> This is the colour when the benzoic acid has been obtained by sublimation; but when the acid has been obtained by the moist way, the colour of the precipitate is brownish yellow.

benzoates, by boiling it in a great deal of water. When dried sect XVIL at 212°, it is anhydrous, and composed of

- 34. Bibenzoated peroxide of iron. When the preceding salt is digested with benzoic acid and water, a solution is obtained, which, when sufficiently concentrated, deposites bibenzoate in yellow crystals, which effloresce in the air, and are partially soluble in water and alcohol.\*
- 35. Subbenzoated peroxide of iron. It is obtained when the neutral salt is boiled in water, or treated with an alkali.
- 36. Gallated peroxide of iron. Gallic acid throws down peroxide of iron from its solution in acid, in the state of a very deep blue powder, the constitution of which has not yet been determined.
- 37. Meconated peroxide of iron. Meconic acid and its salts gives a beautiful red colour to the peroxidized salts of iron, without occasioning any precipitate. Exposure to the light of the sun, or a mixture of protochloride of tin, completely destroys this red colour.
- 38. Boletated peroxide of iron. Boletic acid, or its alkaline salts, precipitate sulphated peroxide of iron, in the state of an aurora red magma.
- 39. Camphorated peroxide of iron. When camphorate of potash is dropt into a persalt of iron, a bulky, light-brown precipitate falls, which is insoluble in water.+
- 40. Suberated peroxide of iron. It may be obtained by double decomposition, in the same way as the preceding salt, which it closely resembles in appearance and properties.
- 41. Pinated peroxide of iron. This salt is obtained when alcoholic solutions of pinic acid and perchloride of iron are mixed together. The tarry precipitate is to be washed with alcohol. A brown, opaque, brittle mass, soluble with difficulty in alcohol, but easily soluble in ether and oil of turpentine.§
- 42. Silvated peroxide of iron. It may be prepared in the same way as the preceding salt. It is but little soluble in alcohol, but very soluble in ether.

<sup>\*</sup> Trommsdorf. † Brandes, Schweigger's Jour. xxxviii. 299.

<sup>‡</sup> Brandes, ibid. xxxiii. 102.

<sup>§</sup> Unverdorben, Poggendorf's Annalen, xi. 235.

<sup>|</sup> Ibid. p. 401.

43. Pyrurated peroxide of iron. A chamois yellow powder.\*

SECTION XVIII. -- SALTS OF PROTOXIDE OF MANGANESE.

Most of the combinations of protoxide of manganese with acids are soluble in water. The solutions are colourless, and have a bitterish and saline taste; by no means so disagreeable as that of most metalline salts. When the solutions are sufficiently concentrated, many of the salts of manganese crystallize. The crystals have a flesh-red colour, which, together with their transparency, gives them a beautiful appearance.

Characters.

- 1. When the solutions of the salts of manganese are treated with fixed alkalies, they deposite a white precipitate, which gradually becomes black when exposed to the air.
- 2. Prussiate of potash occasions a white precipitate when dropped into these solutions.
- 3. Hydrosulphuret of potash occasions a yellowish precipitate. Sulphuretted hydrogen gas gives the solution a white colour, but produces no precipitate, unless the acid be weak.
- 4. Gallic acid and infusion of nut-galls, occasion no precipitate.
- 5. Manganese is not precipitated from its solution in the metallic state by any of the other metals.
- 6. The salts of manganese are not precipitated by succinate or benzoate of ammonia.
- 7. Ammonia produces a white precipitate, which gradually becomes black if air has access. If we add some sal ammoniac, ammonia becomes incapable of throwing down the protoxide of manganese. A solution of sal ammoniac immediately dissolves the precipitate thrown down by ammonia. But on leaving the liquid exposed to the air, the precipitate again appears.
- 8. When a salt of manganese is heated before the blow-pipe with carbonate of soda, it fuses into a green glass, which becomes blueish-green when cold. With borax in the oxidizing flame, it forms an amethyst-coloured glass; but in the reducing flame, the colour disappears.
- 1. Sulphate of manganese. This salt is easily formed, by dissolving the carbonate of manganese in sulphuric acid to saturation, and crystallizing the solution. The crystals are very oblique rhombic prisms, the inclination of the faces being about 148° and 32°. It bears a considerable resemblance to

<sup>\*</sup> Chevallier and Lassaigne, Ann. de Chim. et de Phys. xiii. 161.

the crystalline form of axinite. It is transparent, and has a slight shade of red, which gives it a beautiful appearance. When exposed to the air, it undergoes very little alteration, or becomes only slightly efflorescent. The taste is bitter, and similar to that of glauber salt, but stronger; and, like glauber salt, it may be administered as a cathartic, in doses of from half an ounce to an ounce. Its specific gravity is 2.877. 100 parts of water at the temperature of 40° dissolve 31 parts of this salt previously dried in the temperature of 150°. It is insoluble in alcohol.\* When heated, its water is driven off, and it falls down in the state of a white powder. I found its constituents as follows:

1	atom s	ulphuric	acid	•	•	•	5
1	atom p	rotoxide	of ma	ngan	iese		4.5
5	atoms	water	•	•	•	•	5.625
							15:125

But Mitcherlich (who at first obtained the same quantity of water that I did) has more lately announced that the salt contains only 4 atoms of water. If this statement be correct the atomic weight will be 14. Pfaff makes the water to amount to 7 atoms.

When the solution of sulphate of manganese is concentrated rather too far, a white crust is deposited on the bottom of the vessel. This crust is rather difficultly soluble in water, and is a compound of

1	atom sulphuric	acid	•		5
1	atom protoxide	of man	ganese	•	4.5
3	atoms water	•	. •	•	3.375
					12:875

2. Subsesquisulphate of manganese. Pfaff informs us that by digesting native deutoxide of manganese in sulphuric acid and evaporating the solution, he obtains two different kinds of crystals,—the first kind constitute the crystals of the last species, the other crystals he describes as perfectly white, and composed of doubly oblique four-sided prisms, but not nearly so much so as the preceding salt. He informs us that the constituents of this salt are:

<sup>\*</sup> John, Annals of Philosophy, ii. 183.

<sup>+</sup> Schweigger's Jahrbuch. xxiii. 121.

Class I.	
----------	--

Sulphuric	acid	•	•	•	28.66
Protoxide	of m	angan	ese	•	43.34
Water	•	•	•	•	28.00
					100.00 *

This is equivalent to

1 atom sulphuric acid

1.68 atom protoxide of manganese

4.34 atoms water.

It is doubtful whether it be a disulphate or subsesquisulphate. Were we to adopt the latter opinion, the composition of the salt would probably be

1	atom sulphuric acid	•	•	5
11	atom manganese	•	•	6.78
_	atoms water .	•	•	4.5
				16.05

3. Sulphite of manganese. It may be obtained by digesting carbonate of manganese in liquid sulphurous acid. It is a white granular tasteless powder, not altered by exposure to the air, insoluble in water and alcohol, and decomposed by exposure to a red heat. Its constituents, according to Dr. John, to whom we owe the preceding facts, are

Protoxide of manganese. 40.2

2 Totolide of manganose	•	•	
Acid and water	•	•	<b>59·8</b>
			<del></del>
			100.0
This approaches			
l atom sulphurous acid	•	•	4
1 atom protoxide of mangane	ese	•	4.5
$2\frac{1}{2}$ atoms water	•	•	2.8125
			11.3125

- 4. Hyposulphite of manganese. This salt remains in solution when hyposulphite of lime is precipitated by sulphate of manganese.†
- 5. Hyposulphate of manganese. This salt is very soluble in water, and even deliquescent.‡
- 6. Nitrate of manganese. Nitric acid dissolves manganese with effervescence, occasioned by the emission of nitric gas.

<sup>\*</sup> Schweigger's Jahrbuch. xxiii. 121.

<sup>+</sup> Herschell, Edin. Phil. Jour. i. 24.

<sup>‡</sup> Gay-Lussac; Annals of Philosophy, xiv. 355.

It dissolves the carbonate with facility, but it has very little sect. XVIII. action on the black oxide; however, by very long digestion, it at last dissolves a part of it. The solution goes on much more rapidly if a little sugar or gum, or any similar substance, be added, and at the same time a quantity of carbonic acid gas is emitted. Hence we see that the black oxide must part with a portion of its oxygen before nitric acid can dissolve it. Nitrous acid acts upon the black oxide much more readily, and is converted entirely into nitric acid. The solution, in what manner soever it has been made, is always colourless, provided the manganese be pure.

By dissolving carbonate of manganese in nitric acid and evaporating cautiously, Dr. John obtained nitrate of manganese in needle-form crystals. I have obtained the salt by the same process in prisms. But they are so deliquescent and so difficult of formation that it was impossible to ascertain the exact shape. The crystals have a white colour with a slight shade of red. They have a bitter taste and dissolve readily in water and in alcohol. The alcoholic solution, according to John, burns with a green-coloured flame. The constituents of these crystals, reduced to powder and dried by pressure between folds of blotting paper, I found to be

1 atom nitric acid	•	6.75
1 atom protoxide of manganese	•	4.50
7 atoms water	•	7.875
		$19 \cdot 125$

7. Carbonate of manganese. This salt is easily obtained by pouring an aqueous solution of bicarbonate of potash or soda into sulphate or muriate of manganese, a snow-white powder falls which, when washed and dried, constitutes the carbonate of manganese. It is tasteless and insoluble in water, but easily soluble with effervescence in sulphuric, nitric, or muriatic acid, and the solutions are colourless. It is scarcely possible to preserve it without its colour becoming tinged with yellow owing to the escape of a portion of the carbonic acid and the conversion of the oxide thus abandoned into sesquioxide. When this salt is dried in the open air its constituents, by my analysis, are

1 atom carbonic a	cid	•	•	•	2.75
1 atom protoxide	of ma	ngane	se	•	4.5
2 atoms water		•		-	2.25

Or. Forchhammer, who dried it at a higher temperature, found its constituents to be

1 atom carbonic	acid	•	•	•	2.75
1 atom protoxide	of mar	ngane	se	•	4.5
1 atom water	•	•	•	•	1.125
					8:375

When this salt is heated it loses its carbonic acid and becomes brown or black. When a current of chlorine gas is passed through this salt suspended in water, it gradually loses its carbonic acid and is converted into hydrated deutoxide of manganese. According to John, carbonate of manganese is soluble in 7680 times its weight of water, and in 3840 times its weight of water impregnated with carbonic acid gas. This salt is found native crystallized in obtuse rhomboids with angles of about 107° 20′, according to the measurement of Mr. Brooke, and consequently approaching very near the shape of carbonate of iron.

8. Phosphate of manganese. This salt may be obtained by mixing together solutions of sulphate of manganese and phosphate of soda. It is a white, tasteless, insoluble powder, which melts rather easily when exposed to the heat of a forge; but is very difficult of reduction. According to the analysis of Berthier it is composed of

	Phosphoric acid		•	4.44
2	Protoxide of mangan	ese .	•	5.56
<i>m</i>				10.00 *
This is	almost exactly			
1	atom phosphoric aci	d.	•	4.5
$1_{\frac{1}{4}}$	atom protoxide of m	anganes	se .	5.625
				10.105
				10.125

I am not aware of any other analysis of this salt.

9. Arseniate of manganese. Arsenic acid dissolves the protoxide of manganese with facility; and when it approaches the point of saturation, the solution becomes thick, with small crystals, which separate. These crystals are arseniate of manganese. They are precipitated when an alkaline arseniate is dropped into the solution of manganese in an acid. These crystals do not melt when heated; neither does arsenic sublime, unless charcoal be mixed with them.+

<sup>\*</sup> Jour. de Mines, xxii. 421.

<sup>†</sup> Scheele, i. 188.

I formed this salt by mixing solutions of sulphate of manga- Sect. XVIII.

nese and arseniate of soda. It precipitates under the form of a white tasteless powder, insoluble in water, and producing no change on vegetable blues. It has not been analyzed; but I find that 23.5 grains of the powder dried in the open air lose by ignition 11.25 grains of weight. Hence, if the salt be neutral, the constituents must be

ĺ	atom a	arsenic ac	id				•	7.25
1	atom 1	protoxide	of	manga	anes	е	•	4.5
_	-	water		•		•	•	11.25
								93

- 10. Binarseniate of manganese. This salt, which may be formed by dissolving the preceding one in arsenic acid, is soluble in water. \*
- 11. Borate of manganese. When a solution of borax is poured into a salt of manganese a white precipitate falls. This precipitate is soluble in aqueous sulphate of magnesia. Accordingly it does not appear, when a magnesian salt is mixed with the manganese solution. †
- 12. Silicate of manganese. There are two silicated salts of manganese, which occur native.
- (1.) Silicate of manganese, a beautiful flesh red mineral composed of

1 atom silica 1 atom protoxide of manganese 6.5

- (2.) Disilicate of manganese, a foliated rather dark red mineral, which accompanies Franklinite in New Jersey.
- 13. Selenite of manganese. The neutral salt is a white, soft, insoluble powder. It is very fusible; but preserves its acid very well in close vessels. In the open air, on the contrary, the manganese absorbs oxygen, and allows the acid to make its escape. This salt attacks and corrodes glass much more violently than either the selenite of lime or of magnesia.
- 14. Biselenite of manganese is very soluble in water; by evaporation it yields a crystallizable saline mass. A high temperature drives offhe excess of its acid. ‡
- 15. Antimoniate of manganese. This salt is a white powder not altered by exposure to the air. It is very little soluble
  - # John. + Berzelius.

<sup>‡</sup> Berzelius; Ann. de Chim. et de Phys. ix. 266.

in water. When heated it gives out water and becomes gray. When the heat is carried nearly to redness, combustion takes place, and the salt becomes again white.\*\*

16. Antimonite of manganese. A white matter pretty easily

soluble in water.

- 17. Tellurate of manganese. A white powder not soluble in water.+
- 18. Chromate of manganese. Protoxide of manganese decomposes chromic acid. This salt of course cannot exist.
- 19. Molybdate of manganese. When molybdate of potash is poured into a solution of protoxide of manganese in muriatic acid a brownish white precipitate falls, which is soluble in from 40 to 50 times its weight of water. ‡
- 20. Tungstate of manganese. Tungstic acid and water boiled on powdered manganese convert it into a white powder, as it does likewise the carbonate of manganese. Tungstate of manganese may be obtained by dropping tungstate of potash into a solution of manganese. It is a tasteless white powder, insoluble in water, and not altered by exposure to the air. When heated it becomes yellow, and then brown, but does not melt.
- 21. Oxalate of manganese. This salt may be formed by mixing together rather concentrated solutions of oxalate of potash and sulphate of manganese. No immediate precipitate appears; but after some time the mixture becomes muddy and the salt subsides. It is a very soft tasteless powder, having a white colour with a very slight shade of pink. At is insoluble in water, tasteless, and does not act on vegetable blues. Its constituents, by my analysis, are

22. Acetate of manganese. Acetic acid dissolves carbonate of manganese readily. The solution crystallizes in beautiful rhombic prisms. They have a light reddish colour, are transparent, and not altered by exposure to the air. Their taste is astringent and metallic. They dissolve in  $3\frac{1}{2}$  times their weight of cold water. They are soluble likewise in alcohol.

<sup>\*</sup> Berzelius; Nicholson's Jour. xxxv. 42. † Ibid. † Richter. § John, Gehlen's Jour. xxxv. p. 442.

Their constituents, according to John, are 30 oxide and 70 sect. XVIII. acid and water.\* I found their constituents to be

1 atom acetic acid		•	•	•	6.25
1 atom protoxide	of ma	ngane	ese	•	4.5
4 atoms water	•	•	•	•	4.5
					-
					15.25

23. Lactate of manganese. Flat four-sided prisms, efflorescing in the air, melting when heated in the water of crystallization, and soluble in 12 times its weight of cold water.+

24. Formate of manganese. This salt may be formed by dissolving carbonate of manganese in formic acid. It crystallizes in tables having a reddish colour and falling into powder when gently heated, soluble in 15 times their weight of cold water, but insoluble in alcohol. The taste is sweet and metal-The constituents, according to Göbel, are lic.

1 atom formic a	cid	•	•	•	4.625
1 atom protoxid	e of n	nanga	nese		4.5
1 atom water	•	•	•	•	1.125
					10.25

25. Tartrate of manganese. This salt may be obtained by mixing together solutions of muriate of manganese and tartrate of potash. No immediate change is produced; but on setting the mixture aside beautiful small crystals of tartrate of manganese are deposited. They are four-sided prisms, seemingly

rectangular, end have a flesh-red colour. It is very sparingly soluble in water. Its constituents, by my analysis, are

1 atom tartaric acid		•	•	•	8.25
1 atom protoxide of	mang	gane	se		4.5
2 atoms water	•	•	•	•	2.25

15

- 26. Vinate of manganese. It may be obtained by dissolving carbonate of manganese in vinic acid. The solution when set aside gradually deposites small flesh-red crystals exceedingly similar to the tartrate, and like them very little soluble in water.
- 27. Citrate of manganese. Citric acid dissolves black oxide of manganese with the evolution of carbonic acid gas.‡
- 28. Malate of manganese. Obtained by saturating the acid with carbonate of manganese. A gummy like matter, which does not crystallize, and is very soluble in water.

<sup>\*</sup> Gehlen's Jour. xxxv. p. 440. f Braconnot. # Scheele. II.

- 29. Bimalate of manganese. Obtained by adding malic acid to the solution of the preceding salt. It is a white powder which dissolves in hot water, and forms translucent red crystals. When heated they do not melt, but are gradually decomposed. They are soluble in 41 times their weight of cold water.\*
- 30. Fungate of manganese. A gum like matter not capable of crystallizing.+
- 31. Succinate of manganese. Succinic acid dissolves manganese and its carbonate very readily. The solution has a reddish colour and yields when evaporated crystals which are sometimes four-sided prisms, sometimes four-sided tables, and sometimes octahedrons, composed of two four-sided pyramids applied base to base. These crystals are transparent. appear colourless when viewed singly; but when laid in numbers above each other they assume a rose-red colour. heated they become opaque, white, and similar in appearance to porcelain. They are insoluble in alcohol. At the temperature of 66° they require ten times their weight of water to dissolve them. When distilled they yield water, brown oil, and an According to John they are composed of inflamm ablegas. 30.27 protoxide of manganese, and 69.73 acid and water.t This seems to show that the constituents of the crystals are

1 atom succinic acid	•	•	6.25
1 atom protoxide of manganese	•	•	4.5
3 atoms water	•	•	3.375
			***************************************
			14100

14.125

32. Benzoate of manganese. Benzoic acid dissolves manganese and its carbonate slowly. The solution yields thin prismatic crystals, which are colourless, transparent, and are not altered by exposure to the air. They have a sweetish astringent taste, which leaves a bitterish impression. At the temperature of 66°, they require 20 times their weight of water to dissolve them. They are soluble likewise in alcohol. When distilled they yield a very little water, but a good deal of oil. According to John they are composed of 24 oxide and 76 acid and water. It is obvious from this that the salt is anhydrous, and that its constituents are

1 atom benzoic acid	•	•	15
1 atom protoxide of manganese	•	•	4.5
			19.5

<sup>\*</sup> Braconnot. † Ibid. ‡Gehlen's Jour. x.p. 439. § Ibid. p. 438.

- 33. Camphorate of manganese. Camphorate of soda occa- Sect. XIX. sions no precipitate in the salts of manganese. But when carbonate of manganese is boiled with camphoric acid, camphorate of manganese is formed. When the solution is left to spontaneous evaporation, the salt crystallizes in plates which are very soluble in water.\*
- 34. Suberate of manganese may be obtained by the same process as the preceding salt. It does not crystallize, but by spontaneous evaporation may be obtained in a yellowish-white translucent matter, having the lustre of enamel. It is soluble Its taste is sweet, saline, and astringent, and has a good deal of resemblance to suberate of magnesia.†
- 35. Pinate of manganese. It may be obtained by precipitating sulphate of manganese by pinate of potash. It is a gray powder, which agglutinates into a resinous like mass, at the heat of boiling water. It dissolves in ether, but not in water nor alcohol. The alcohol separates a portion of the pinic acid-t
- 36. Silvate of manganese dissolves easily in absolute alcohol. The colourless solution becomes brown by exposure to the air, and deposites brown manganese.§
- 37. Sulphonaphthalate of manganese. It constitutes a neutral crystallizable salt. The taste is slightly austere. soluble in water and alcohol, and is decomposed by heat.

## SECTION X1X.-SALTS OF SESQUIOXIDE OF MANGANESE.

These salts have been very little examined, and indeed are almost unknown. Their colour is reddish, and so far as I know they cannot be obtained in a neutral state, or in crystals. The few facts which I have observed are the following:

1. Sulphated sesquioxide of manganese. When concentrated sulphuric acid is poured over sesquioxide of manganese, reduced to an impalpable powder, and the mixture is left to digest at the common temperature of the atmosphere, we obtain a violetblue liquid, which when diluted with water, becomes carmine-red, and by still farther dilution, blood-red. be concentrated somewhat in a gentle heat without alteration, but if we boil it oxygen is disengaged, and the liquid becomes nearly colourless. Alcohol reduces it to the state of common sulphate of manganese when assisted by a moderate heat. This solution cannot be neutralized nor obtained in crystals.

<sup>\*</sup> Brandes, Schweigger's Jour. xxxviii. 299. † Ibid. xxxiii. 103.

<sup>‡</sup> Unverdorben, Poggendorf's Annalen, xi. 232. § Ibid. p. 400.

Faraday, Annals of Philosophy (2d series), xii. 210.

- Class I. When the acid is dilute the same saline solution is obtained, but the quantity of oxide dissolved is less. When we boil deutoxide of manganese in dilute sulphuric acid, oxygen gas is given out, and we obtain a red solution containing common sulphate of manganese, mixed with sulphated sesquioxide.
  - 2. Nitrated sesquioxide of manganese cannot be formed.
  - 3. Oxalated sesquioxide of manganese. When oxalate of potash is dropt into sulphated sesquioxide of manganese, a rosered coloured precipitate falls, which is probably oxalated sesquioxide.
  - 4. Carbonated sesquioxide of manganese. An alkaline carbonate throws down from the same solution a reddish-brown powder.
  - 5. Tartrated sesquioxide of manganese. When sesquioxide of manganese in the state of a fine powder is digested in tartaric acid without the application of heat, a dark brown solution is obtained with a shade of yellow.
  - 6. Citrated sesquioxide of manganese. Citric acid when digested in the same way gives a similarly coloured solution.

## SECTION XX.—SALTS OF PROTOXIDE OF NICKEL.

The soluble salts of nickel have a beautiful emerald-green colour, while that of the insoluble salts is usually light green, though in some cases it is leek-green.

Characters.

- 1. Prussiate of potash when dropt into the solution of these salts, throws down a milk-white precipitate.
  - 2. The hydrosulphuret of potash occasions a black precipitate.
  - 3. Sulphuretted hydrogen gas occasions no precipitate.
- 4. Gallic acid, and the infusion of nut-galls, occasion no precipitate, at least in the sulphate of nickel.
  - 5. The ammoniacal solution of oxide of nickel has a blue colour.
- 6. Potash throws down an apple-green precipitate, not redissolved by adding an excess of the alkali.
- 7. Carbonate of ammonia throws down an apple-green precipitate redissolved in an excess of the carbonate, rendering the liquid bluish-green.
- 8. The greater number of the salts of nickel when heated with borax before the blow-pipe, fuse into an orange-yellow or reddish glass, which becomes yellow or almost colourless on cooling. When the quantity of salt of nickel is considerable, compared to the borax, the glass is opaque, and of a dull brown while in fusion; but on cooling it becomes dull red and transparent.

Sect. XX.

1. Sulphate of nickel. This salt is easily formed by dissolving carbonate of nickel in dilute sulphuric acid, and concentrating the solution. When the solution contains an excess of acid the crystals are rectangular prisms with square bases. When the solution is neutral the crystals are usually right rhombic prisms, very nearly the same as the form of sulphate The inclination of the lateral faces of the prism to each other is 91° 10', according to the measurement of Mr. Brooke.\* The colour of this salt is a fine deep emerald-green. Its taste is styptic and slightly acrid, and it remains long in the. mouth. At the temperature of 60°, 100 parts of water dissolve 75.6 parts of these crystals. When exposed to the air the rhombic prisms lose a little water, but this does not happen to the square prisms.+ When heated they swell up but do not melt, and they assume a yellow colour when the water is driven off. The salt may be heated to incipient ignition without losing any acid. It has been repeatedly analyzed with nearly the same result by different chemists. Its constituents are

1 atom sulphuric acid	•	•	5
1 atom protoxide of nickel			4.25
7 atoms water	•	•	7.875
			17.125

Mr. Phillips found in the square prism about two per cent. of the water replaced by sulphuric acid.‡ How far this replacement is the cause of the different form of the crystals is not clear.

- 2. Disulphate of nickel. When the preceding salt is mixed with a quantity of potash not sufficient to decompose it completely, a green powder is precipitated which constitutes the present salt. It is very little soluble in water, and possesses alkaline properties.
- 3. Nitrate of nickel. Carbonate of nickel dissolves readily in nitric acid; the solution, when sufficiently concentrated, deposites crystals of nitrate of nickel in very flat four-sided oblique prisms, of an emerald-green colour, not quite so fine as that of sulphate of nickel. They dissolve in twice their weight of cold water. They are soluble also in alcohol. When heated they give out water. When exposed to the air they either deliquesce or effloresce according as they want or retain

<sup>\*</sup> Annals of Philosophy (2d series) vi. 438.

<sup>†</sup> Cooper, Ibid. p. 438. ‡ Ibid. p. 440.

Class I.	their	water	of	crystallization.	The	constituents	of	this	salt,
1	accor	ding to	m	y analysis, are as	follo	ws:			

1 atom nitric acid	•	•	6.75
1 atom protoxide of nickel	•	•	4.25
5 atoms water	•	•	5.625
			<del></del>

4. Subnitrate of nickel. This salt was first obtained by Proust. His method was to heat the preceding salt cautiously in a retort till it assumed a yellowish-green colour. It is insoluble in water, and composed, according to Proust, of 12 nitric acid, and 88 protoxide of nickel.\* This approaches

1 atom nitric acid	•	•	6.75
11 atoms oxide of nickel	•	•	46.75
	•		
			£9.50

5. Carbonate of nickel. This salt is obtained by precipitating a solution of sulphate of nickel by carbonate of soda, washing the precipitate, and drying it in the open air. It is a light apple-green powder, nearly tasteless, and not sensibly soluble in water, but dissolving with effervescence in acids. Its constituents are

1 atom carbonic acid	•	•	2.75
1 atom protoxide of nickel	•	•	4.25
3 atoms water	•	•	3.375
			10:375

6. Subcarbonate of nickel. This salt was obtained by Berthier, by precipitating sulphate of nickel by a bicarbonate of potash. The precipitate is greenish-white, pulverulent, and very light. He found its constituents to be

			100.0†
Water	•	•	30.7
Protoxide of nickel	•	•	48.3
Carbonic acid	•	•	21

# This approaches

1 atom carbonie acid	•	•	2.19
$1\frac{1}{2}$ atom protoxide of nickel	•	•	6.375
$3\frac{1}{2}$ atoms water	•	•	3.9375

13.0925

16.625

<sup>\*</sup> Ann. de Chim. lx. 273.

<sup>+</sup> Ann. de Mines, iv. 481.

While he	found the	constituents	of the	carbonate	of	nickel	Sect. XX.
thrown dow	n by carb	onate of soda	to be				

Carbonic acid	•	•	14
Protoxide of nickel	•	•	47.5
Water	•	•	<b>38·5</b>
÷			100*
This is a near approximation to			
1 atom carbonic acid	r	•	2.75
2 atoms protoxide of nickel	•	•	<b>8·5</b>
7 atoms water	•	•	<b>7·875</b>

19·125

According to these analyses the last of these salts is a dicarbonate, and the first a subsesquicarbonate of nickel.

7. Phosphate of nickel. This salt is obtained when sulphate of nickel and phosphate of soda are mixed together in the requisite proportions, after being dissolved in water. After washing and drying on the filter, it is a light pea-green powder, tasteless, adhering to the tongue, and insoluble in water. 11.375 grains of it when exposed to a red heat lost 3.375 grains of its weight. Hence I consider it as a compound of

1 atom phosphoric acid	•		4.5
l atom protoxide of nickel	•	•	4.28
3 atoms water	•		3.375

T2·155

8. Arseniate of nickel. This salt is obtained when solutions of arseniate of soda and sulphate of nickel are mixed together. The arseniate of nickel, while moist, has a light green colour; but when dried on the filter the colour deepens to a dark leekgreen. It is tasteless, and insoluble in water, yet it slightly reddens vegetable blues. When heated to the temperature of about 500°, it gives out two-thirds of its water, and becomes dark brownish-yellow. In a red heat it loses the whole of its water, and becomes dark-brown. Its constituents are

l atom arsenic acid	•	•	7.25
I atom protoxide of nickel	•	•	4.25
6 atoms water	•	•	6.75
			18.25

<sup>\*</sup> Ann. de Mines, iv. p. 482.

9. Binarseniate of nickel. When arsenic acid is digested upon carbonate of nickel, no apparent action is perceptible for some time; but in a few days the liquid assumes a fine green colour, and the portion of carbonate of nickel undissolved acquires the peculiar shade of green, which characterizes arseniate of nickel while moist. The liquid, when filtered and concentrated yields no crystals, but a yellowish-green matter is deposited, rather bulky, and having a good deal of clamminess. When dried by pressure between folds of blotting paper it is insoluble in water, has a slightly acid taste, and reddens vegetable blues powerfully. Hence it is probably a binarseniate of nickel. Judging from the water given off when it is heated, its constituents are

2 atoms arsenic acid	•	•	14.5
1 atom protoxide of nickel	•	•	4.25
10 atoms water		•	11.28

30.03

7.95

10. Diarseniate of nickel. This salt occurs as a frequent coating on the arsenietted nickel of Allemont in the department of the Isere in France, sometimes in apple-green compact masses, and sometimes in a greenish-white friable crust. It is usually mixed with a little arseniate of cobalt. According to the analysis of Berthier, its constituents appear to be

2 atoms oxide of nickel	•		8.5
	•	•	0 0
5 atoms water.	•	•	$\boldsymbol{5.625}$
			21:375*

- 11. Borate of nickel. Borax throws down from nickel salts a light apple-green powder insoluble in water, but soluble in sulphuric, nitric and muriatic acids. It melts before the blowpipe into a hyacinth-red glass. Boracic acid has no action on
- 12. Selenite of nickel. The neutral salt is an insoluble powder, white while moist; but becoming pale apple-green when dried. The biselenite is soluble, and gives a green matter resembling gum.†
- 13. Antimoniate of nickel. A greenish-white powder, not soluble in water.
  - 14. Chromate of nickel. When solutions of chromate of
    - \* Ann. de Mines, iv. 472.

metallic nickel.

I atom arsenic acid

<sup>†</sup> Berzelius, Ann. de Chim. et de Phys. ix. 339. 

‡ Berzelius.

potash and sulphate of nickel are mixed together no precipitate appears at first, but a reddish-brown powder gradually falls, the quantity of which is increased by concentrating the liquid. This deposite, when washed and dried, is rather a beautiful reddish-brown powder, destitute of taste, and not affecting vegetable blues. Its constituents are

1 atom chromic a	cid		•	$6 \cdot 5$
1 atom protoxide	of nick	el	•	4.25
4 atoms water	•	•	•	4.5
				1 - 0 -

15. Molybdate of nickel. Molybdic acid precipitates nitrate of nickel white, provided there be no excess of nitric acid.\*

16. Oxalate of nickel. This salt may be obtained by mixing solutions of sulphate of nickel and oxalate of ammonia in the atomic proportions. For some minutes the liquid retains its transparency, but by degrees it becomes opaque, and oxalate of nickel is slowly deposited. This salt when well washed and dried in the air is a light green powder, destitute of taste, and insoluble in water. Its constituents are

1 atom oxalic acid	d .	•	•	4.5
1 atom protoxide	of nick	el		4.25
4 atoms water	•	•	•	4.5
				13.25

From the experiments of Tupputi, it appears that when heated it loses the half of its water. It dissolves in the mineral acids, but is very little soluble in oxalic acid.

17. Acetate of nickel. Carbonate of nickel dissolves readily in acetic acid. The saturated solution is dark green. When set aside it gradually deposites acetate of nickel in light green crystals. They are rhomboids, but the salt has a great tendency to concrete at the bottom of the vessel without assuming any regular form. This salt is very soluble in water, but insoluble in absolute alcohol. Its taste is at first sweetish, but it leaves an impression in the mouth like that of sulphate of zinc, but much weaker. When heated it does not melt, but gives out water mixed with a little acetic acid, and gradually assumes a yellowish green colour. It then takes fire and burns like tinder, leaving oxide of nickel. The constituents of this salt are

1 atom acetic acid	•	6.25
1 atom protoxide of nickel	•	4.25
5 atoms water	•	<b>5</b> ·625
		16.125

- 18. Lactate of nickel. Irregular emerald-green crystals, having a taste at first sweet, and then metallic. They contain but little water. When heated they do not melt, but are decomposed and burn. They are soluble in 30 times their weight of cold water.\*
- 19. Formate of nickel. Green needles, which when heated become first yellow, then black.+
- 20. Tartrate of nickel. This salt may be obtained by dissolving carbonate of nickel in tartaric acid. When the green coloured solution thus obtained is evaporated to dryness, a light olive-green powder is obtained, which is tasteless, insoluble in water, and producing no alteration on vegetable blues. It is anhydrous, and composed of

1 atom tartaric acid . 8.251 atom protoxide of nickel

12.5

- 21. Citrate of nickel. Obtained by boiling citric acid with carbonate of nickel. Greenish flocks of a weak metallic taste, soluble in the mineral acids and in citric acid. ‡
- 22. Pyromucate of nickel. Pyromucate of soda precipitates nitrate of nickel apple-green.§
- 23. Succinate of nickel. Succinate of soda throws down nitrate of nickel apple-green.
- 24. Benzoate of nickel. A green coloured salt, which does not crystallize, but may be obtained in plates. It reddens litmus paper, is soluble in water, and also in alcohol. ate of ammonia does not precipitate nitrate of nickel.\*\*
- 25. Oleate of nickel. It is obtained when hot solutions of oleate of potash and sulphate of nickel are mixed together. separates very slowly from the liquid in which it is generated. It has a beautiful greenish-yellow colour.++
- 26. Pinate of nickel. It is obtained by precipitating sulphate of nickel by pinate of potash. A green, porous, resinous-looking mass. Its solution in oil of turpentine when boiled becomes
  - \* Braconnot. † Arfvedson. ‡ Tupputi. § Trommsdorf. ¶ Ibid. | Ibid. \*\* Hisinger. †† Chevreul, sur les corps gras, p. 96.

From this solution absolute alcohol throws down a Sect. XXI. brown tar-looking matter. The salt dissolves readily in ether and oil of turpentine, and the solution has a green colour.\*

- 27. Aspartate of nickel. A green, brittle matter, which does not crystallize.+
- 28. Sulphonaphthalate of nickel may be obtained by dissolving carbonate of nickel in sulphonaphthalic acid. It has a green colour, crystallizes, and is decomposed by heat, like the other sulphonaphthalates: ‡

## SECTION XXI. -- SALTS OF PROTOXIDE OF COBALT.

The salts of cobalt chiefly attracted the attention of chemists, in consequence of the property which some of them have of changing their colour when heated, and thus forming what has received the name of sympathetic ink; an appellation given to all liquids, the characters formed by which are colourless and invisible when written upon paper, but become visible and coloured by undergoing certain processes; and likewise to those liquids which form characters upon paper susceptible of changing their colour by certain processes. The salts of cobalt may be distinguished by the following properties:

- 1. The greater number of them are soluble in water, and the characters. solution has a reddish colour, at least when the salts are neutral.§
- 2. The alkalies, when dropped into these solutions, occasion a blue-coloured precipitate.
  - 3. Prussiate of potash occasions a light-green precipitate.
- 4. Hydrosulphuret of potash occasions a black precipitate, soluble again if the hydrosulphuret be added in excess. Sulphuretted hydrogen gas occasions no precipitate in these solutions.¶
- 5. Gallic acid produces no change, but the tincture of nutgalls occasions a yellowish-white precipitate.
- 6. The ammoniacal solution of oxide of cobalt has the colour of port wine. It is not immediately precipitated by prussiate of potash, but after some time a reddish precipitate falls.
  - \* Unverdorben, Poggendorf's Annalen, xi. 237.
  - + Plisson, Ann. de Chim. et de Phys. xl. 314.
  - ‡ Faraday, Annals of Philosophy (2d series), xii. 210.
- § The solution of cobalt in muriatic acid, when concentrated, has a blue or bluish-green colour as long as there is an excess of acid.
- | When the cobalt is contaminated with arsenic acid, or when it is dissolved in arsenic acid, the precipitate by alkalies is reddish-brown.
  - ¶ Proust, Ann. de Chim. xxxv. 54.

- Class 1.
- 7. The salts of cobalt are not precipitated by hydriodate of zinc.
- 8. Cobalt is not precipitated from its solution in acids by zinc.
- 9. Carbonate of ammonia throws down a red precipitate, which is soluble in sal ammoniac.
- 10. The greater number of the salts of cobalt, when melted before the blow-pipe with borax, form a transparent blue coloured bead.
- 1. Sulphate of cobalt. This salt may be obtained by dissolving carbonate of cobalt in dilute sulphuric acid, and concentrating the solution till it deposites crystals. It has a deep carmine-red colour, and crystallizes in oblique rhombic prisms, having very nearly the same shape as sulphate of iron. The inclination of the base to either side of the prism is, by Mr. Brooke's measurement, 99° 45′, and that of two contiguous faces of the prism 82° 20′.\* The crystals have a somewhat sharp, bitterish, and metalline taste. They are transparent, but when heated they give out water and become opaque without melting. According to Proust, they may be exposed to a red heat without losing their acid. They dissolve in 24 times their weight of cold water. In alcohol they are insoluble. Their constituents are as follows:

1 atom sulphuric acid .	•	5
1 atom protoxide of cobalt		4.25
7 atoms water	•	7.875

## 17.125

2. Bisulphate of cobalt. When sulphate of cobalt is crystallized in an excess of acid, long four-sided prisms are obtained, having a red colour, and efflorescing on the surface without falling to powder when exposed to the air. They are composed of

2 atoms sulphur	ic acid	•	•	10
1 atom protoxid	e of coba	ılt	•	4.25
3 atoms water	•	•	٠.	3.375
				17.625

3. Subsulphate of cobalt. When a solution of sulphate of cobalt is mixed with a quantity of alkali insufficient to decompose it completely, a flesh-red precipitate falls, which constitutes a subsulphate of cobalt. It is insoluble in water.+

<sup>\*</sup> Annals of Philosophy (2d series), vi. 120. † Berzelius.

4. Hyposulphate of cobalt. This salt may be obtained by sect. XXI. decomposing sulphate of cobalt by means of hyposulphate of barytes. The filtered liquid when concentrated yields indistinct crystals of hyposulphate of cobalt. They have a rose-red colour, are very soluble in water, but do not deliquesce. Their constituents are

1 atom hyp	osulphu	ric aci	d	•	9
1 atom prot				•	4.25
6 atoms wat		•	•	•	6.75
			•		20*

5. Nitrate of cobalt. This salt is easily obtained by dissolving cobalt or its oxide in nitric acid. The solution when sufficiently concentrated deposites crystals of nitrate of cobalt. These crystals have a brownish-red colour, and are very ill defined, but seem to be rhomboids. Their taste is acrid and bitter, and they redden vegetable blues. They dissolve readily in water, and deliquesce rather rapidly when exposed to the air. When heated, they melt and give out water, and when the heat is increased nitric acid fumes are given off, and at last a black matter (peroxide of cobalt) only remains. The constituents of this salt are as follows:

1	atom 1	nitric aci	.d	•	•	6.75
1	atom '	protoxid	e of col	balt	•	4.25
6	atoms	water	•	•	•	6.75
						17.75

When the dry nitrate of cobalt is heated it becomes blue, but again recovers its red colour when allowed to cool.

6. Carbonate of cobalt. This salt may be obtained by precipitating nitrate of cobalt by carbonate of soda, washing the precipitate, and drying it on a filter. It is a light powder, having a pink colour, and no great depth of shade. It is tasteless, insoluble in water, and not altered by exposure to the air, but soluble in the alkaline carbonates when dissolved in water. Its constituents are as follows:

1 atom	n carbonic a	acid	•	•	2.75
1 atom	protoxide	of col	balt	•	4.25
1 atom	water	•	•	•	1.125
					8.125

<sup>\*</sup> Heeren, Poggendorf's Annalen, vii. 190.

7. Phosphate of cobalt. This salt may be obtained by digesting carbonate of cobalt in phosphoric acid, and mixing the solution with alcohol. It is gelatinous, and has a fine crimson colour. When dried, it concretes into a hard dark-red matter, which reddens vegetable blues. Its constituents are probably

1 atom phosphori	ic acid		•	4.5
1 atom protoxide	of col	oalt	•	4.25
2 atoms water	•	•	•	2.25

11

8. Arseniate of cobalt. When solutions of nitrate of cobalt and arseniate of soda are mixed and evaporated, the arseniate of cobalt falls in the state of a crimson coloured jelly, which, when washed and dried, assumes the form of scales. It is light, and has a fine crimson colour. It is tasteless, and does not alter the colour of vegetable blues.

This salt is found native, sometimes in the state of a fine red efflorescence, and sometimes crystallized in small four-sided

prisms or tables.

When the arseniate of cobalt is heated in a glass tube it becomes violet, but is not decomposed, nor does it tinge the glass blue. It dissolves in nitric acid without effervescence. When its solution in muriatic acid is mixed with sulphuretted hydrogen, it does not become turbid till it has stood two hours. Potash precipitates blue oxide of cobalt, and combines with the acid.\*

The constituents of this salt seem to be

l atom arsenic a	cid	•	•	7.25
1 atom protoxide	e of col	balt	•	4.25
4 atoms water	•	•	•	4.5
				16

- 9. Borate of cobalt. Boracic acid does not act upon cobalt, but it precipitates that metal from its solution in other acids in the state of a reddish-white powder. This borate is scarcely soluble in water. When heated it melts into a deep blue glass.+
- 10. Silicate of cobalt. When a solution of silicate of soda is mixed with a solution of a salt of cobalt a fine blue precipitate falls, which when dried, becomes very light coloured.

<sup>\*</sup> Proust, Ann. de Chim. lx. 271.

<sup>†</sup> Wenzel's Verwandtschaft, p. 258.

- 11. Selenite of cobalt. The neutral selenite is an insoluble red coloured powder. The biselenite leaves when evaporated a red beautiful shining varnish.\*
- 12. Antimoniate of cobalt. This salt is obtained by dropping antimoniate of potash into a salt of cobalt. It is a red coloured precipitate, which gradually contracts and assumes the form of crystalline grains. It is soluble in water, but not very much so. According to Berzelius, it is composed of

Antimonic acid	•	•	•	<b>52</b>
Oxide of cobalt	•	•	•	14
Water	•	•	•	33.3
	-			99.3

This (if we reckon the atom of antimonic acid 21) is equivalent to

1 atom antimonic acid, 1.36 atom protoxide of cobalt,

1:2 atom water.

Shall we consider the true constitution to be

1	atom	antimonic	acio	i.	•	21
$1\frac{1}{3}$	atom	protoxide	of c	obalt		5.666
ľ	atom	water	•	•	•	1.125
						_

**27·793**?

- 13. Antimonite of cobalt. A bulky lilac-coloured precipitate having no aspect of crystallization. It is pretty soluble in water. It contains 25 per cent. of water of crystallization.
- 14. Chromate of cobalt. This salt is obtained by mixing together solutions of chromate of potash and nitrate of cobalt. The chromate gradually falls down in the state of a reddishbrown coloured powder. It has no taste, and produces no change on vegetable blues. 12.85 grains of it ignited assumed an olive-green colour, and lost 2.1 gr. of weight. Hence, I consider it as a compound of

1 atom chromic	acid	•	•	<b>6·5</b>
1 atom protoxide	e of col	balt	•	4.25
2 atoms water	•	•	•	2.25
				<u>≰</u>
				13

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 339.

<sup>†</sup> Nicholson's Journal, xxxv. 42. 

‡ Berzelius, ibid. 45.

Class L

- 15. Molybdate of cobalt. A dirty-yellow powder, assuming a red colour when dried, and decomposed both by acids and alkalies.\*
- 16. Oxalate of cobalt. It may be obtained by mixing together solutions of nitrate of cobalt and oxalate of ammonia. The precipitate may be collected on a filter, well washed and dried in the open air. It is a light red powder, destitute of taste, insoluble in water, and incapable of altering the colour of vegetable blues. Its constituents are

1 atom oxalic ac	id .	•	•	4.5
1 atom protoxid	e of col	oalt	•	4.25
2 atoms water	•	•	•	2.25
				11

It scarcely dissolves in oxalic acid.

- 17. Acetate of cobalt. Acetic acid dissolves the oxide of cobalt with facility. The solution does not crystallize; and when evaporated to dryness, soon deliquesce again. It has a fine red colour while cold, but becomes blue when heated.† This solution forms a sympathetic ink: the characters drawn in it are nearly colourless, or light red while cold, but become blue when heated.‡
- 18. Lactate of cobalt. Lactic acid readily dissolves the protoxide of cobalt. The solution is red, and when evaporated deposites crystalline crusts. The crystalline grains do not appear to contain any water of crystallization. They dissolve in 83 times their weight of water at 70°. When heated they do not melt but become black, take fire, and leave oxide of cobalt.§
- 19. Formate of cobalt. Rose-red indistinct crystals. When heated they become first blue, then black. They dissolve with difficulty in water, and not at all in alcohol.
- 20. Tartrate of cobalt. When solution of tartaric acid is digested over protoxide of cobalt, a fine crimson solution is obtained, which when concentrated, lets fall a precipitate, having a most beautiful crimson colour. This precipitate, which is tartrate of cobalt, is slightly soluble in water, it has little or no taste, but it reddens vegetable blues. Its constituents are

<sup>\*</sup> Berzelius. † Wenzel's Verwandtschaft, p. 150.

Isleman, Crell's Annals, 1785, ii. 25.

Braconnot, Ann. de Chim. lxxxvi. 89.

Arfvedson.

l atom tartaric acid	•	•	8.25	Sect. XXII.
1 atom protoxide of cobalt	•	•	4.25	**************************************
2 atoms water	•	•	2.25	
			14.75	

21. Succinate of cobalt. Succinate of soda when dropt into a concentrated solution of sulphate of cobalt, throws down a light red precipitate.

22. Benzoate of cobalt. The salts of cobalt are not precipitated by benzoate of ammonia or of potash. According to Tromsdorf, benzoic acid dissolves a very little of the carbonate of cobalt. The solution crystallizes like the pure acid.

- 23. Oleate of cobalt. This may be obtained by mixing hot solutions of cleate of potash and sulphate of cobalt together. The soap takes a long time to separate from the liquid in which it is formed. Its colour is greenish-blue at first; but it gradually becomes green. But Chevreul is of opinion that the true colour of this soap is blue.\*
- 24. Pinate of cobalt. When nitrate of cobalt is mixed with pinate of potash, a blue precipitate falls, which may be agglutinated by heat. It dissolves in ether with a blue colour.+

## SECTION XXII. -- SALTS OF OXIDE OF ZINC.

Almost all the acids act with energy on zinc, in consequence of the strong affinity which it has for oxygen. The salts of zinc, therefore, are very easily formed; and as the metal forms only one oxide, they are not liable to change their state, like the salts of iron and tin. They may be distinguished by the following properties:

- 1. The greater number of them are soluble in water, and characters. the solution is colourless and transparent.
- 2. Prussiate of potash occasions a white gelatinous precipitate when dropped into these solutions.
- 3. Hydrosulphuret of potash and sulphuretted hydrogen gas occasion a white precipitate.
- 4. Gallic acid and the infusion of nutgalls occasion no precipitate when dropped into these solutions.
- 5. Potash occasions a white gelatinous presipitate, which is readily dissolved by sulphuric or muriatic acid, and by an excess of potash. Ammonia behaves in the same manner.

<sup>\*</sup> Sur les corps gras, p. 96.

<sup>+</sup> Unverdomin, Poggendorf's Annalen, xi. 235.

- 6. Zinc is not precipitated in the metallic form by any of the other metals.
- 7. Sulphocyanate of potash and hydriodate of potash occasion white precipitates when dropped into a solution of a salt of zinc.
- 8. Carbonate of potash throws down a white precipitate, not soluble in an excess of the carbonate. But it may be dissolved by potash or ammonia.
- 9. When a zinc salt is heated before the blow-pipe on charcoal, after the acid is destroyed or dissipated, the remaining oxide of zinc being reduced, gives out a brilliant light, and is gradually dissipated before the reducing flame, a white vapour condensing at the same time on the surface of the charcoal.
- 1. Sulphate of zinc. This salt, according to the best accounts, was discovered at Ramelsberg, in Germany, about the middle of the 16th century. Many ascribe the invention to Julius, Duke of Brunswick. Henkel and Neumann were the first chemists who proved that it contained zinc; and Brandt first ascertained its composition completely.\* It is generally formed for commercial purposes from sulphuretted zinc, or blende, as it is called by mineralogists. This ore is roasted, which converts the sulphur into an acid; it is then dissolved in water, and concentrated so much that, on cooling, it crystallizes very rapidly and forms a mass not unlike loaf-sugar. This salt is usually called white vitriol. It is almost always contaminated with iron, and often with copper and lead. Hence the yellow spots which are visible on it, and hence also the reason that its solution in water lets fall a dirty brown sediment; a circumstance very much complained of by surgeons when they use that solution in medicine. It may be easily purified by dissolving it in water, and putting into the solution a quantity of zinc filings; taking care to agitate it occasionally. The zinc precipitates the foreign metals, and takes their place. solution is then to be filtered, and the sulphate of zinc may be obtained from it in crystals by proper evaporation.

The crystals are right rhombic prisms, deviating very little from rectangular, for the inclination of the two contiguous faces of the prism is 91° 7′. The lateral edges of the prism are often replaced by tangent planes, and the crystals often terminate in pyramidal summits. The shape is precisely the same

<sup>\*</sup> Beckman's History of Inventions, art. Zinc.

<sup>+</sup> See the measurement by Brooke, Annals of Philosophy (2d series), vi. 437.

as that of the rhombic prisms of sulphate of nickel. The crys- Sect. XXII. tals are large and transparent, and colourless, they redden vegetable blues, and have a peculiar and very disagreeable metalline The specific gravity when crystallized is, by my experiments, 1.980. At the temperature of 60° 100 grains water dissolve 93.88 grains of the crystal. Boiling water dissolves any quantity whatever. When heated, it melts and speedily loses its water of crystallization, and, in a high temperature, loses part of its acid. The constituents of this salt are

1 atom sulphuric acid	•	•	5
1 atom oxide of zinc		•	5.25
7 atoms water	•	•	7.875
			19.195

When the solution of this salt is too much concentrated it deposites on cooling a white solid crust, not so soluble in water as the crystals, and composed of

1 atom sulphuric acid	•	•	5
I atom oxide of zinc	•	•	<b>5</b> ·2 <b>5</b>
3 atoms water	•	•	3.375
	-		13.625

When this salt is strongly heated it loses the whole of its acid and water, and the oxide of zinc remains behind in a state of purity. Probably pure sulphuric acid might be easily obtained by distilling this salt. For it parts with the whole of its water before the acid begins to separate.

2. Tris-sulphate of zinc. When the preceding salt is boiled with zinc or its oxide, or when a quantity of potash is added to the solution, not sufficient to decompose the whole salt, in either case, white scales are obtained having considerable lustre, very little soluble in hot, and not at all in cold water. scales, according to Vogel, are composed of

1 atom sulphuric acid	•	•	5
3 atoms oxide of zinc	•	•	15.75
			90.75

3. Sulphite of zinc. Sulphurous acid dissolves the oxide of zinc with the evolution of heat, but without effervescence. The solution yields crystals of sulphite of zinc. These crystals have a less acrid, but more styptic taste than the following. species. They are less soluble in water, and more easily crystallized. They are insoluble in alcohol. When exposed to

Class I. the air they are very soon changed into sulphate of zinc; whereas the subsulphite remains long unchanged.

4. Subsulphite of zinc. When a current of sulphurous acid is passed through water, containing fragments of zinc, the metal is gradually dissolved without effervescence. When the solution is evaporated it becomes thick like honey, and deposites long slender crystals in the form of four-sided prisms, terminated by four-sided pyramids. These are crystals of subsulphite of zinc. They are soluble in water and in alcohol, When exposed to the air they become white, and deposite a white insoluble powder. Before the blow-pipe the salt swells, emits a brilliant light, and forms dendritical ramifications. When distilled, it yields water, sulphurous acid, sulphuric acid, and sulphur; and there remain behind, oxide of zinc and a little sulphate of that metal. Sulphuric, nitric, and muriatic acids, when poured into its solution in water, drive off sulphurous acid, while a quantity of sulphur precipitates. The theory of the formation of this salt is obvious. The sulphurous acid gives out half of its oxygen to oxidize the zinc. So that the salt (abstracting the water) is a compound of

I atom subsulphurous acid	•	•	3
1 atom oxide of zinc	•	•	5.25
			8.25

5. Hyposulphate of zinc. Obtained by mixing solutions of hyposulphate of barytes, and sulphate of zinc. The filtered solution, when concentrated, deposites irregular crystals of hyposulphate of zinc. They are not altered by exposure to the air; their taste is very harsh and disagreeable, and they are very soluble in water. Their constituents, according to the analysis of Heeren, are as follows:

1 atom hyposulphuric acid	•	•	9
1 atom oxide of zinc	•	•	5.25
6 atoms water	•	•	6.75
			-
			01*

6. Nitrate of zinc. Nitric acid attacks zinc with prodigious violence, and has been said even to inflame it. It is necessary to moderate its action by using it in a diluted state: even then considerable heat is evolved, and a strong effervescence is occasioned by the escape of nitrous oxide gas.

<sup>\*</sup> Poggendorf's Annalen, vii. 183.

The solution is transparent and colourless, very caustic, and yields by evaporation flat striated tetrahedral prisms, terminated by four-sided pyramids. The specific gravity of these crystals is 2.096.\* They attract moisture very rapidly when exposed to the air. They are very soluble both in water and alcohol. When heated they melt and detonate on burning coals, emitting a red flame. When distilled, they emit red vapours of nitrous acid, and assume a gelatinous form. In a strong heat they are decomposed completely, giving out nitrous

1 atom nitric acid		•	6.75
1 atom oxide of zinc	•	•	5.25
6 atoms water	•	•	6.75
			<del></del>
			18.75

gas and oxygen gas. The constituents of this salt are

7. Octakinitrate of zinc. This salt may be obtained by evaporating the solution of the preceding salt nearly to dryness, or by pouring a small quantity of ammonia into it. It is a white powder, insoluble in water, and composed, according to the analysis of Grouvelle, of

	Nitrie acid	•	•	•	19.79
	Oxide of zinc		•	•	81.69
	Water .	•	•	•	4.56
This same		.: 41.			100†
I his corre	esponds nearly w				
	l atom nitric	acid	•	•	6.75
	8 atoms oxide	of z	inc	•	42
	2 atoms water	•	•	•	2.25
					<del></del>

The zinc is rather less than 8 atoms; but the deficiency does not amount to  $\frac{1}{4}$ th atom, or one sixteenth part of the whole.

51

8. Chlorate of zinc. This salt may be obtained by dissolving carbonate of zinc in chloric acid. The carbonic acid is disengaged; but it is difficult to saturate the chloric acid with oxide of zinc. This salt has a very astringent taste: when evaporated to the consistence of a syrup, it crystallizes in low octahedrons. Its solution in water does not precipitate

<sup>\*</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

<sup>†</sup> Ann. de Chim. et de Phys. xix. 137.

Class 1.

nitrate of silver. On burning coals it fuses and produces a yellow light, but does not detonate. When mixed with sulphuric acid it assumes an orange-red colour, and produces a slight effervescence; but the chloric acid is not decomposed. For when the mixture is diluted with water, it does not precipitate sulphate of silver.\*

Chloric acid dissolves zinc without effervescence. It would appear from the experiments of Vauquelin that the solution is a mixture of chlorate of zinc and chloride of zinc. When a current of chlorine gas is made to pass through water, having carbonate of zinc diffused through it, the same two compounds appear to be formed.†

- 9. Iodate of zinc. This salt may be formed by dissolving carbonate of zinc in iodic acid. It may be procured also by mixing with a soluble iodate a solution of sulphate of zinc, not too much concentrated. After an interval of some hours the iodate of zinc precipitates in spherical grains. This salt is but little soluble in water. It deflagrates on coals, but much more feebly than iodate of potash.
- 10. Carbonate of zinc. This salt may be obtained by mixing solutions of sulphate of zinc and carbonate of soda in the atomic proportions. It is a fine, white, tasteless powder, insoluble in water, but soluble with effervescence in acids. When simply dried by exposure to the air, its constituents, according to the analysis of Smithson, are

1 atom carbonic acid . 2.75 1 atom oxide of zinc . 5.25 3 atoms water . 3.375

# 11.375

This salt occurs native, and was confounded by the older mineralogists with several other species, under the name of calamine. It occurs crystallized in obtuse rhomboids, octahedrons, and four-sided prisms, and is anhydrous.

11. Dicarbonate of zinc. When sulphate of zinc is precipitated by a solution of sesquicarbonate of soda, little or no effervescence takes place. The precipitate is white, and in a very minute state of division. Its constituents, according to the analysis of Boussingalt, are

<sup>\*</sup> Vauquelin, Ann. de Chim. xcv. 116.

<sup>+</sup> Ibid.

<sup>‡</sup> Gay-Lussac, Ann. de Chim. xci. 85.

		_	
Carbonic acid .	•	19	Sect. XXII.
Oxide of zinc .	•	70	
Water	•	11	
		100*	
This is nearly equivalent to			
l atom carbonic acid	i.	2.75	
2 atoms oxide of zin	ic .	10.5	
$l_{\frac{1}{2}}$ atom water .	•	1.6875	
		14.9375	
12. Hydrous dicarbonate of zi	inc.	This salt occurs native	·,
and is composed of			
l atom carbonic acie	d.	<b>2·75</b>	
2 atoms oxide of zir	ic .	10.50	

13. Phosphate of zinc. When carbonate of zinc is introduced into phosphoric acid it is dissolved with effervescence, and a biphosphate of zinc formed as when the metal is employed. But if we boil the liquid over carbonate of zinc, after it refuses to take up any more in the cold, the whole is gradually converted into a tough magma, which becomes very hard when cold. It softens when heated, and, if we urge the fire, abundance of nitrous gas is given out. The substance thus obtained is a phosphate of zinc. It is a tasteless white matter, insoluble in water. Before the blow-pipe it readily melts into a transparent colourless glass. Phosphate of zinc is composed of

2 atoms water .

1 atom phosphoric acid . 4.50 1 atom oxide of zinc . 5.25

9.75

2.25

15.5

14. Subsesquiphosphate of zinc. When solutions of phosphate of soda and sulphate of zinc are mixed together, the liquid becomes acid, and a white powder falls. It is tasteless, insoluble in water, and fuses easily into a colourless glass. When this salt is dried by simple exposure to the air, its constituents are

<sup>\*</sup> Ann. de Chim. et de Phys. xxix. 284.

1	atom phosphoric acid		4.5
	atom oxide of zinc	•	7.875
3	atoms water .	•	3.375
•	*		
	•		15.75

15. Biphosphate of zinc. When carbonate of zinc is dissolved in an excess of phosphoric acid, and the solution evaporated, a gum-like mass is obtained, soluble in water, and easily melting into a transparent, colourless glass.\*

16. Subsesquiarseniate of zinc. When sulphate of zinc and arseniate of soda are mixed together, the liquid becomes acid, while a transparent, gelatinous precipitate falls. When dried in the open air, it assumes the appearance of enamel. It is tasteless, insoluble in water, and does not affect vegetable blues. Its constituents are

1 atom arsenic a	cid		7.25
$1\frac{1}{2}$ atom oxide of	zinc	•	7.875
9 atoms water	•	•	10.125
			25.25

- 17. Binarseniate of zinc. When zinc or its oxide is dissolved in an excess of arsenic acid, the solution, when concentrated, yields cubic crystals of binarseniate of zinc.
- 18. Borate of zinc. Boracic acid scarcely attacks zinc; but it combines with its oxide, and forms with it an insoluble borate of zinc. This salt may be precipitated in a white powder, by pouring borate of soda into the nitrate or muriate of zinc; or by mixing boracic acid with liquid sulphate of zinc. When strongly heated, this borate becomes yellow, and is at last converted into an opaque slag.†
- '19. Silicate of zinc. This salt occurs native, and is known by the name of electric calamine. It is white, tasteless, and insoluble in water, and crystallized in right rhombic prisms, whose faces are inclined to each other at angles of 102° 35'. Its constituents are

20. Selenite of zinc. The neutral salt is a crystalline powder, insoluble in water. When heated, it gives out its water

Wenzel.

of combination. It then melts and becomes yellow and transparent. But on cooling it resumes its white colour. Its surface and fracture are crystalline. At a white heat it lets a portion of its acid escape, and is converted into a subselenite, which undergoes no farther alteration from the fire.

The biselenite is very soluble in water; when evaporated, it leaves a transparent matter like gum.\*

- 21. Antinoniate of zinc. This salt is obtained when antimoniate of potash is dropped into a solution of sulphate of zinc. It is a white powder, having a crystalline appearance when dried. It is soluble to a certain degree in water. When heated, it gives out its water of crystallization, and becomes yellow. It is not reduced by the blow-pipe upon charcoal.
  - 22. Tellurate of zinc. A white insoluble powder.
- 23. Dichromate of zinc. This salt is obtained when solutions of sulphate of zinc and chromate of potash are mixed in the atomic proportions. It falls in the state of a fine yellow powder; slightly soluble in water. It is an anhydrous salt, composed of

1 atom chromic acid . 6.5 2 atoms oxide of zinc . 10.5

17

The resulting compounds, when chromate of potash and sulphate of zinc are mixed, are curious. Let us suppose 16 atoms of each of these salts mixed. The five following new salts are produced:

- 1. 6 atoms dichromate of zinc
- 2. 5 atoms bichromate of potash
- 3. 4 atoms potash-sulphate of zinc
- 4. 6 atoms sulphate of potash
- 5. 1 atom bisulphate of potash

6 atoms chromic acid, 12 atoms oxide of zinc.

§ 10 atoms chromic acid,

5 atoms potash.

8 atoms sulphuric acid,

4 atoms potash,

4 atoms oxide of zinc.

6 atoms sulphuric acid,

6 atoms potash.

2 atoms sulphuric acid,

l atom potash.

All of these salts may be easily obtained by crystallizing the liquid, except the last, which, from its small quantity, could not be recognised.

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 265.

<sup>†</sup> Ibid. Nicholson's Journal, xxxv. 42.

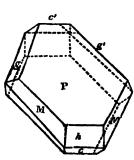
24. Molybdate of zinc. Obtained by mixing solutions of molybdate of ammonia and sulphate of zinc. A yellowish-white powder, not easily dissolved in water, but soluble in the strong mineral acids. According to the analysis of Brandes, it is composed of

1 atom molybdic acid . 9
1 atom oxide of zinc . 5.25

25. Tungstate of zinc. A white powder, insoluble in water. 26. Oxalate of zinc. This salt may be formed by mixing together solutions of oxalate of ammonia and sulphate of zinc in the atomic proportions. For a few seconds the mixture continues transparent, but it gradually becomes muddy, and deposites oxalate of zinc in abundance. It is a white, tasteless powder, insoluble in water, but soluble in muriatic acid and ammonia. According to Dulong, it loses all its water at 212°, and when heated more strongly, all the acid is driven off, and the oxide of zinc remains. Its constituents are

12

27. Acetate of zinc. Acetic acid readily dissolves zinc, and



yields by evaporation crystals of acetate of zinc, which were first mentioned by Glauber. This salt has a bitter metallic taste. The crystals are thin, talcy plates, with a silky lustre. They are rhomboidal, and, according to Mr. Brooke,\* the primary form is an oblique rhombic prism, as represented in the margin. The measurements of which are as follows:

P on M or M	[′	•	112° 28′
M on M'		•	67 24
P on h	•	•	133 30
P on c	•	•	100 00
P on c'	•	•	80 00
Pongorg'			<b>75 30</b>

This salt is very soluble in water. When thrown upon live

coals, it burns with a blue flame. When distilled, it yields sock XXII. water, an inflammable liquid, and some oil, and towards the end of the process oxide of zinc sublimes.\* It is apt to lose a little of its acid by keeping. Its constituents are as follows:

 1 atom acetic acid
 .
 6.25

 5 atom oxide of zinc
 .
 5.25

 7 atoms water
 .
 7.875

19.375

- 28. Lactate of zinc. Lactic acid dissolves zinc with effervescence, and the salt formed is capable of crystallizing.† The crystals have the figure of four-sided prisms, terminated by oblique summits. At the temperature of 70° they dissolve in 50 times their weight of water, and they are more soluble in boiling water.‡
- 29. Formate of zinc. This salt may be obtained by dissolving zinc in formic acid. It crystallizes in colourless transparent cubes, soluble at 66° in 24 times its weight of water, and is soluble in alcohol. When heated, it swells, then fuses, giving out fetid vapours, and leaving oxide of zinc. Its constituents, according to the analysis of Göbel, are as follows:

1 atom formic acid . 4.625
1 atom oxide of zinc . 5.25
2 atoms water . 2.25

12.125

30. Tartrate of zinc. Tartaric acid attacks zinc with effervescence, and forms with it a salt difficultly soluble in water.§ It is a white, tasteless powder like chalk, which is anhydrous, and composed of

> 1 atom tartaric acid . 8.25 1 atom oxide of zinc . 5.25

> > 13.5

- 31. Vinate of zinc. The aqueous solution of vinic acid dissolves zinc readily with the evolution of hydrogen gas. The vinate of zinc is gradually deposited in white needles. The solution, when concentrated, deposites more of these needles. This salt fuses easily when heated.
  - 32. Citrate of zinc. Citric acid attacks zinc with efferves-

+ Scheele, ii. 65.

<sup>\*</sup> Monnet.

<sup>‡</sup> Braconnot, Ann. de Chim. Ixxxvi. 91.

<sup>§</sup> Dijon Academicians.

<sup>|</sup> Walchner.

cence, and gradually deposites small brilliant crystals of citrate of zinc. They are insoluble in water, and have a styptic and metallic taste.

33. Malate of zinc crystallizes in right four-sided prisms, which redden litmus paper. It dissolves in 55 times its weight of cold water, and in 10 times its weight of boiling water. If we reckon the atomic weight of malic acid 9.5, this salt, according to the analysis of Braconnot, is composed of

1 atom malic acid . 9.5 1 atom oxide of zinc . 5.25  $1\frac{1}{2}$  atom water . 1.6875

16.4375

- 34. Fungate of zinc. It crystallizes in parallelopipeds, is moderately soluble in water, and is decomposed by heat without swelling up.\*
- 35. Pyromucate of zinc. It may be obtained by dissolving zinc in pyromucic acid. It does not crystallize, but may be obtained by evaporation in a solid mass.†
- 36. Succinate of zinc. Succinic acid dissolves zinc with effervescence, and the solution yields long slender foliated crystals, the properties of which have not been examined. The salts of zinc are not precipitated by succinate of soda.
- 37. Benzoate of zinc. Zinc is readily dissolved by benzoic acid. The solution yields needle-shaped crystals, which are soluble in water and alcohol. When exposed to heat, their acid is volatilized.§ The salts of zinc are not precipitated by benzoate of ammonia.
- 38. Camphorate of zinc. Obtained by double affinity. A white powder.
- 39. Suberate of zinc. Suberate of ammonia throws down this salt from the saline solutions of zinc. A white, soft, tasteless powder. When heated it becomes yellow, when further heated it melts and is decomposed.
- 40. Oleate of zinc. It may be obtained by mixing hot solutions of oleate of potash and sulphate of zinc. It is white, and melts below the temperature of 212°.\*\*
  - 41. Butyrate of zinc. Butyric acid diluted with water dis-

\* Braconnot. † Labillardiere.

‡ Wenzel's Verwandtschaft, p. 240.

§ Trommsdorf, Ann. de Chim. xi. 317.

\*\* Chevreul, sur les corps gras, p. 94.

solves the carbonate of zinc with effervescence. The solution sect. XXIII. always reddens litmus paper, however long the digestion be continued. When concentrated, it deposites crystals of butyrate of zinc in brilliant plates. They have the smell and taste of butyric acid. When the solution of this salt is evaporated, a portion of the acid escapes, and a white matter is deposited, which is a sub-butyrate of zinc.\*

- 42. Cholesterate of zinc. It may be obtained by double affinity, has a fine red colour, and is but little soluble in water.
- 43. Pinate of zinc. Obtained by mixing solutions of pinate of potash and sulphate of zinc. Yellowish-brown flocks, fusing when heated. It is insoluble in water and alcohol, but dissolves in ether, linseed oil, and oil of turpentine. An alcohol solution of pinic acid when boiled over oxide of zinc gradually combines with it.‡
- 44. Silvate of zinc. Soluble in 15 times its weight of cold absolute alcohol, and in a smaller quantity of the same liquid when hot. In other respects it resembles silvate of lime.
- 45. Aspartate of zinc. It crystallizes in small white points, is opaque, and does not absorb moisture from the air. Has the peculiar taste which characterizes the aspartates, followed by the flavour of zinc salts.
- 46. Sulphonaphthalate of zinc. Zinc is readily acted on by sulphonaphthalic acid, hydrogen gas being evolved, and the oxide of zinc dissolved. The salt formed is moderately soluble in hot water. When the solution cools an abundant crop of needle-form crystals is obtained. These crystals are white, unaltered by exposure to the air, have a bitter taste, and burn with flame, leaving sulphate of zinc.¶
- 47. Vegetosulphate of zinc. Vegetosulphuric acid dissolves zinc with effervescence.\*\*

### SECTION XXIII. - SALTS OF OXIDE OF CADMIUM.

This genus of salts, as far as it has been hitherto examined, may be distinguished by the following characters.

- 1. A considerable number of them are soluble in water. Characters. The aqueous solutions are colourless, or have a very slight
  - \* Chevreul, sur les corps gras, p. 132.
  - + Pelletier and Caventou.
  - † Unverdorben, Poggendorf's Annalen, xi. 232. § Ibid. p. 401.
  - Plisson, Ann. de Chim. et de Phys. xl. 314.
  - ¶ Faraday, Annals of Philosophy, (2d series), xii. 210.
  - \*\* Braconnot, Ann. de Chim. et de Phys. xii. 186.

- yellow shade. The insoluble salts of cadmium are white powders.
  - 2. When a fixed alkali is dropped into a solution of cadmium, the oxide is precipitated in the state of a white hydrate, and is not again redissolved by adding an excess of the precipitant.
  - 3. Ammonia likewise precipitates it in the state of a white hydrate. The precipitate is again redissolved, when an excess of ammonia is added.
  - 4. The alkaline carbonates throw down cadmium in the state of a white carbonate. This carbonate does not form a hydrate, as is the case with the carbonate of zinc. Neither is it redissolved by the addition of an excess of carbonate of ammonia, as is the case with the carbonate of zinc, unless there existed a notable excess of acid in the solution before the addition of the carbonate of ammonia.
  - 5. Phosphate of soda throws down cadmium in the state of a white powder, while zinc is thrown down by the same precipitant in the state of crystalline scales.
  - 6. Sulphuretted hydrogen gas, and the hydrosulphurets precipitate cadmium yellow or orange. This precipitate resembles orpiment, but may be distinguished by the facility with which it dissolves in muriatic acid, and by its bearing a red heat without being altered.
  - 7. Prussiate of potash throws down cadmium from its solutions white.
    - 8. Infusion of nut-galls does not occasion any precipitate.
  - 9. A plate of zinc, when put into a solution of cadmium, throws down that metal in a reguline state in dendritical leaves.
  - 1. Sulphate of cadmium. This salt crystallizes in large transparent rectangular prisms, very similar in appearance to sulphate of zinc, and very soluble in water. It effloresces strongly when exposed to the air, and is deprived of its water of crystallization by the application of a low heat, without undergoing previous liquefaction, as is the case with sulphate of zinc. The crystals redden vegetable blues. It is not easily decomposed by the fire, and bears a low red heat without undergoing any change. In a strong red heat sulphuric acid is given out, and it is changed into a subsulphate which crystallizes in plates, and is difficultly soluble in water.

The crystals are four-sided prisms, apparently rectangular. Two of the opposite edges of the prism are often replaced by tangent planes. The constituents of this salt are as follows:

l atom sulphuric acid .	•	5
1 atom oxide of cadmium	•	8
4 atoms water	•	4.5
		17.5

Sect. XXIII.

- 2. Hyposulphate of cadmium. A solution of cadmium in hyposulphuric acid left to spontaneous evaporation, deposites a saline matter having a very disagreeable taste, very soluble in water, and deliquescing in a moist atmosphere.\*
- 3. Nitrate of cadmium. This salt crystallized in the vacuum of an air-pump over sulphuric acid constitutes thin transparent plates. It crystallizes also, according to Stromeyer, in prisms and needles cohering and constituting a radiated mass. It is very soluble in water, and speedily deliquesces when exposed to the air. Its constituents are

4. Carbonate of cadmium. Easily obtained by double affinity. It is a white, tasteless powder, insoluble in water, and having some resemblance to carbonate of lead. It is destitute of combined water, but when dried in the open air retains about 2 per cent. of water, obviously hygrometrically lodged in the salt. Its constituents are

1 atom carbonic acid . . 2.75
1 atom oxide of cadmium . 8

5. Phosphate of cadmium. This salt may be obtained by mixing solutions of nitrate of cadmium and phosphate of soda. The precipitate is at first very bulky, but it afterwards diminishes very much in volume. From a comparison between my own experiments on this salt, and the analysis of it by Stromeyer, it would seem to be a compound of

1 atom phosphoric acid . 4.5  $1\frac{1}{4}$  atom oxide of cadmium . 10.0  $1\frac{1}{2}$  atom water . . . 1.6875

16.1875

6. Arseniate of cadmium. When arseniate of soda is added

<sup>\*</sup> Heeren, Poggendorf's Annalen, vii. 183.

Class	I.
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to a solution of nitrate of cadmium a white precipitate falls, at fire very bulky, but in a few hours it contracts much in size. This precipitate is a white powder, insoluble in water. It has not been analyzed, but if it be neutral, its constituents must be

ĺ	atom	arseni	c acid	•	•	<b>7·25</b>
1	atom	oxide	of cad	mium	•	8
$\frac{1}{2}$	atom	water	•	•	•	1.6875
						16.9375

7. Borate of cadmium. This salt is a white powder scarcely soluble in water, and after having been exposed to a red heat its constituents, according to Stromeyer, are

Boracic acid .	•	•	•	27.8847
Oxide of cadmium	•	•	•	72-1153
m				100.0000
This is obviously				
1 atom boracic acid	•	•		3
1 atom oxide of cadr	nium	•	•	8
				11

8. Chromate of cadmium. This salt may be obtained by mixing solutions of sulphate of cadmium and chromate of potash. It falls in the state of a beautiful yellow powder, which has little or no taste and yet is not absolutely insoluble in water. Its constituents are

1 atom chromic acid	•	•	<b>6.5</b>
1 atom oxide of cadmium	•	•	8
5 atoms water .	•	•	5.625
			00.105

9. Molybdate of cadmium. When molybdate of ammonia is mixed with sulphate of cadmium a grayish white powder falls, which becomes brown when gently ignited.\*

10. Oxalate of cadmium. Obtained by mixing solutions of oxalate of potash and nitrate of cadmium. A white tasteless powder insoluble in water. Its constituents are

1 atom oxalic aci	d	•	•	•	4.5
1 atom oxide of	cadmii	um	•	•	8
3 atoms water	•	•	•	•	3.375
A					15.875

11. Acetate of cadmium. When a very concentrated solution of this salt is exposed for about ten days to the air its gradually converted into a crystalline mass, while a thick liquid remains floating above it. The crystals are prisms very soluble in water, and not altered by exposure to the air. They are composed of

1 atom acetic ac	eid .	•	•	6.25
1 atom oxide of	cadmium	•	•	8.00
2 atoms water		•	•	2.25

16.5

12. Formate of cadmium. Obtained by digesting carbonate of cadmium in formic acid. Crystals, cubes, and rhomboidal dodecahedrons, of a sweetish, astringent, and metallic taste. It loses its water with difficulty when heated, but is at last decomposed, leaving oxide of cadmium. Its constituents, according to the analysis of Göbel, to whom we are indebted for the examination of this salt, are as follows:

1 atom formic acid		•	•	•	4.625
1 atom oxide of ca	dmi	um	•	•	8
2 atoms water	•	•	•	•	2.25

14.875

13. Tartrate of cadmium. If tartrate of potash in slight excess be added to a solution of nitrate of cadmium there instantly falls a pretty bulky precipitate. The liquid separated from this precipitate deposites at the end of 24 hours a small quantity of transparent granular crystals. The supernatant liquor gives a slight precipitate with carbonate of soda. Hence tartrate of cadmium is slightly soluble in water. These crystals are tasteless and composed of

1 atom tartaric aci	ď	•	•	•	8.25
1 atom oxide of ca	dmiu	m	•	•	8.00
2 atoms water	•	•	•	•	2.25

18.5

14. Succinate of cadmium. Cadmium is very little soluble in succinic acid, but carbonate of cadmium dissolves very readily. By evaporation transparent prisms are obtained, which dissolve readily in water, and which, when treated with alcohol, are decomposed into a bisalt soluble in alcohol, while a neutral salt remains undissolved.\*

II.

<sup>\*</sup> John.

15. Citrate of cadmium. Citrate of ammonia produces a remarkably bulky gelatinous precipitate in nitrate of cadmium, which is white and scarcely soluble in water. Its constituents are

1 atom citric acid		•	7.25
1 atom oxide of cadmium	٠.	•	8.00
2 atoms water .		•	2.25
			17.5

### SECTION XXIV. -- SALTS OF PROTOXIDE OF LEAD.

The salts of lead were formerly distinguished by the name of saturn, the title by which lead was known among the alchymists. The protoxide only of this metal seems capable of combining with acids so as to form salts. These bodies may be distinguished by the following properties:

Characters.

- 1. A considerable number of them are scarcely soluble in water without an excess of acid. These before the blow-pipe on charcoal yield very readily a button of lead.
- 2. The solution of the soluble salts of lead in water is generally colourless and transparent.
- 3. They have almost all less or more of a sweet taste, accompanied with a certain degree of astringency.
- 4. Prussiate of potash occasions a white precipitate when poured into solutions containing salts of lead.
- 5. Hydrosulphuret of potash occasions a black precipitate. The same precipitate is produced by sulphuretted hydrogen.
- 6. Gallic acid and the infusion of nut-galls occasion a white precipitate.
- 7. A plate of zinc kept in a solution of lead occasions either a white precipitate, or the lead appears in its metallic state.
- 8. When potash is dropt into a solution of a salt of lead a white powder falls, which is redissolved by adding an excess of the potash.
- 9. When chromate of potash is dropt into a solution of lead a beautiful orange precipitate falls.
- 1. Sulphate of lead. Sulphuric acid does not attack lead while cold; but at a boiling heat it communicates a portion of its oxygen, sulphurous acid gas is emitted, and the whole is converted into a thick white mass, which is sulphate of lead. It may be obtained readily by pouring sulphuric acid into acetate of lead, or by mixing this last salt with any of the alkaline sulphates. The sulphate of lead precipitates in the state

of a white powder. This salt is tasteless. It is insoluble in alcohol and in nitric acid. According to Kirwan, it requires 1200 parts of water to dissolve it; \* but when it contains an excess of acid, it is more soluble, and yields by evaporation small white crystals, which, according to Sage, have the form of tetrahedral prisms. It dissolves in strong muriatic acid when the action of the solvent is promoted by heat; the solution, on cooling, deposites many crystals of muriate of lead.+

This salt occurs native in transparent colourless crystals having the diamond lustre and a specific gravity of 6.3. The primary form of the crystal is a right rhombic prism, whose contiguous faces are inclined at angles of 103° 42′. But it frequently occurs in octahedrons and other shapes easily deducible from the primary crystal. It is anhydrous; though it usually contains a little hygrometrical water. Its constituents are

I atom sulphuric acid		•	5
1 atom protoxide of lead	•	•	14
			19

- 2. Disulphate of lead. According to Vauquelin when the preceding salt is digested in ammonia it loses half its acid and is converted into disulphate.
- 3. Sulphite of lead. Sulphurous acid has no action whatever on lead. It absorbs oxygen from the red oxide of that metal, and is converted into sulphuric acid. But it combines with the protoxide of lead, and forms with it a sulphite, which is in the state of a white powder, insoluble in water, and tasteless. Before the blow-pipe on charcoal it melts, becomes yellow, and the lead is at last reduced. When exposed to a red heat, it loses 5 per cent. of its weight; sulphurous acid exhales; and there remains a blackish mass composed of sulphate of lead and sulphuret. When treated with nitric acid, the sulphuret is decomposed, and crystals of nitrate obtained. Its constituents are

l atom sulphurous acid	•	•	4
1 atom protoxide of lead	•	•	14
			10

- 4. Hyposulphite of lead. This salt is obtained by pouring nitrate of lead into the solution of any hyposulphite. A white
  - \* Mineralogy, ii. 211. + Descotils, Nicholson's Jour. xii. 221.

<sup>‡</sup> Fourcroy and Vauquelin, Connoissances Chimiques, vi. 86.

precipitate falls which is at first redissolved; but upon adding the requisite quantity of nitrate it becomes permanent. This hyposulphite is a white mealy powder, which leaves an impression of sweetness when held long in the mouth. At a heat under 212° it turns black, and when the heat is raised it takes fire, becoming red hot, and burns with a weak flame. If it be now removed from the fire, the ignition and combustion may be maintained for any length of time by cautiously adding small quantities of the substance. When heated in a retort it loses 20 per cent. of its weight, which is pure sulphurous acid gas. When fully ignited, the loss is 20.6 per cent. the residuum, which is a black powder, is, according to Mr. Herschell, a sulphuretted oxide of lead. The constituents of hyposulphite of lead, according to the analysis of Mr. Herschell, are as follows:

Hyposulphurous acid	•	•	29.7
Oxide of lead .	•	•	70.3
This is obviously			100.0
1 atom hyposulphurous acid			5
1 atom protoxide of lead			14
-			
			19

5. Hyposulphate of lead. This salt may be obtained by dissolving carbonate of lead in hyposulphuric acid, and leaving the solution to spontaneous evaporation. Large transparent crystals are obtained, the form of which is not easily described, but they have been figured and measured by Heeren, who considers the primary form to be a bipyramidal dodecahedron.\* The taste of the salt is very sweet and astringent, and it is very soluble in water. Its constituents, according to the analysis of Heeren, are

1 atom hyposulphuric acid	•	•	9
1 atom oxide of lead	•	•	14
4 atoms water	•	•	4.5
			27.5

6. Dihyposulphate of lead. This salt may be obtained by mixing the solution of the preceding with a quantity of ammonia not sufficient to decompose it completely. Soft white needles fall which react as an alkali. When digested in nitric

<sup>\*</sup> Poggendorf's Annalen, vii. 183.

acid they are converted into sulphate of lead, a portion of oxide sect. XXIV. of lead being at the same time dissolved. When exposed to the air a portion of the oxide of lead is converted into carbonate.\* It is but sparingly soluble in water.

7. Decahyposulphate of lead. When the preceding salt is digested in an excess of ammonia it is converted into a soft white powder, reacting as an alkali, and very little soluble in water. It is decomposed by carbonic acid. Its constituents, according to the analysis of Heeren, are

Hyposulphuric acid .	•	•	5
Protoxide of lead .		•	81
Water	•	•	14
			100
This approaches			
l atom hyposulphuric acid	•	•	9
10 atoms protoxide of lead	•	•	140
22 atoms water	•	•	24.75

173.75

8. Nitrate of lead. Nitric acid acts upon lead with considerable energy, provided it be not too much concentrated; first converting it into a white powder, which is a subnitrate, and then dissolving it, especially when assisted by heat. The yellow oxide of lead is dissolved by nitric acid completely, and without effervescence; but the red oxide is rendered white; <sup>6</sup>/<sub>7</sub>ths of its weight are dissolved, and <sup>1</sup>/<sub>7</sub>th is converted into brown oxide, and remains undissolved. †

The solution is transparent and colourless, and when sufficiently concentrated deposites crystals of nitrate of lead. If the liquor contains an excess of acid these crystals are transparent and colourless, but if it be neutral they are opaque and white, and have a pearly lustre. The shape is usually the regular octahedron, sometimes the cube, the cubo-octahedron, and the tetrahedron, or various modifications of these forms. The taste of these crystals is sweet and austere. They are not altered by exposure to the air. They are soluble in 7.6 parts of boiling water.‡ The crystals dissolve in alcohol. Their specific gravity is 4.068. § When heated they decrepitate, and then undergo a kind of detonation, emitting very

<sup>\*</sup> Heeren, Poggendorf's Annalen, vii. 186. † Proust.

<sup>#</sup> Wenzel's Verwandtschaft, p. 310.

<sup>§</sup> Hassenfratz, Ann. de Chim. xxviii. 12. By my trials, 3.954.

brilliant sparks.\* When they are triturated with sulphur in a hot mortar, a feeble detonation is produced, and the lead is reduced to the metallic state.† The constituents of this salt are

1 atom nitric acid . . . 6.75
1 atom protoxide of lead . . . 14
20.75

Iron occasions no precipitate though kept in the solution of nitrate of lead. ‡

9. Dinitrate of lead. This salt was obtained by Chevreul by boiling a mixture of equal weights of nitrate of lead and protoxide of lead, filtrating the liquid while hot, and allowing it to crystallize in close vessels. On cooling it deposited crystals in pearl-coloured scales. The taste of this salt is sweet and astringent. When a current of carbonic acid gas is passed through its solution, it is converted into common nitrate and carbonate of lead. There can be no doubt, from the analysis of Berzelius and Chevreul, that this salt contains just double the quantity of base that exists in the nitrate. Hence its constituents are

10. Trisnitrate of lead. This salt was obtained by Berzelius by precipitating nitrate of lead with a quantity of ammonia not sufficient to decompose it completely. It is a white powder. When gently heated it loses its water and becomes yellow; but again assumes a white colour on cooling. Slightly soluble in pure water. Its constituents, deduced from the analysis of Berzelius, are

1 atom nitric acid..6.753 atoms protoxide of lead..42 $1\frac{1}{2}$  atoms water..1.6875

50.4375

11. Hexanitrate of lead. This salt may be obtained by the same process as the preceding, but the precipitate is to be digested for some time in ammonia. A white powder having a slightly astringent taste. It is insoluble in water, and when

<sup>\*</sup> Bergman, ii. 470. † Van Mons, Ann. de Chim. xxvii. 81.

<sup>‡</sup> Wenzel's Verwandtschaft, p. 90.

heated leaves protoxide of lead. Its constituents, by Berze- sect. XXIV. lius' analysis, are

 1 atom nitric acid
 .
 6 75

 6 atoms protoxide of lead
 .
 84

 1 atom water
 .
 1.125

 91.875
 .

12. Hyponitrite of lead. Berzelius obtained this salt by dissolving dihyponitrite of lead in water of the temperature of 167°, adding as much sulphuric acid as would deprive it of half the lead, filtering and evaporating spontaneously. Octahedral crystals of a deep yellow colour are deposited. It is more soluble in water than nitrate of lead. When the solution is heated to 212° deutoxide of azote is given out and the salt is changed into trisnitrate of lead. When the solution is left exposed to the air oxygen is absorbed and the salt is changed into nitrate of lead.

Its constituents, as determined by the analysis of Berzelius, are

1 atom hyponitrous acid	•	•	4.75
1 atom protoxide of lead	•	•	14.00
1 atom water	•	•	1.125
			19.875

13. Dihyponitrite of lead. This salt was discovered by Proust; but its true composition was first ascertained by Berzelius\* and Chevreul.† Wenzel had indeed obtained it, but at the time when his experiments were made it was impossible to draw the proper inference.‡

When a solution of nitrate of lead is boiled upon lead in the metallic state, the lead is gradually oxidized at the expense of the acid, which partly flies off in the state of nitrous gas, and is partly converted into hyponitrous acid. If the requisite portion of lead only is dissolved, which, according to the experiments of Berzelius, amounts to 7.8 parts of lead for every 10 parts of nitrate of lead employed, the solution has a yellow colour and deposites dihyponitrite of lead in scales.

This salt crystallizes in plates or scales and has a yellow colour. 100 parts of water at the temperature of 74° dissolve 1.26 of this salt; 100 parts of boiling water dissolve 9.41 parts. When this solution is allowed to cool it retains more of the salt than cold water would be able to dissolve. This solution

<sup>\*</sup> Ann. de Chim. lxxxiii. 5. † Ibid. 67. ‡ Verwandtschaft, p. 90.

has a yellow colour. It restores the blue colour of litmus paper reddened by an acid. It does not absorb oxygen from the atmosphere; but when exposed to the air it becomes covered with a pellicle of carbonate of lead. When this salt in powder is thrown into nitric acid or acetic acid, nitrous fumes are disengaged. When a current of carbonic acid is passed through the solution of this salt in water, it would appear from Chevreul's experiments that one-half of the oxide of lead is thrown down in the state of carbonate. The other half remaining, combined with the nitrous acid, constitutes hyponitrite of lead.

The constituents of this salt, as determined by the analysis of Berzelius, are

1 atom hyponitrous acid	•	•	. <b>4·75</b>
2 atoms protoxide of lead	•	•	28
2 atoms water	•	•	2.25
			35

14. Tetrahyponitrite of lead. When I part of nitrate of lead, 50 parts of water, and  $1\frac{1}{2}$  part of thin plates of lead are digested for 36 hours in a temperature between 160° and 176°, this salt is obtained. It sometimes crystallizes during the digestion, and sometimes only after the liquid is allowed to cool in tile-red needles. It reacts strongly as an alkali; is not altered by exposure to the air. When heated it gives out first water, then its acid, and protoxide of lead only remains. It is soluble in 140 times its weight of cold water, and 33 times its weight of boiling water. Its constituents, as determined by the analysis of Berzelius, are

Hyponitrous acid	•	•	7·7 <b>4</b>
Protoxide of lead	•	•	90.38
$\mathbf{Water}$	•	•	1.88
ant to Suturb			100.00
This is obviously			
1 atom hyponitrous acid	•	•	4.75
4 atoms protoxide of lead	•	•	<b>56</b>
1 atom water	•	•	1.125
			61.875*

<sup>15.</sup> Chlorate of lead. This salt may be formed by dissolving

<sup>\*</sup> The analysis of Chevreul, and the earlier analysis of Berzelius, would make this salt a trishyponitrate.

litharge in fine powder in chloric acid. The solution has a very sweet and astringent taste. When left to spontaneous evaporation it deposites brilliant crystalline plates. On burning coals it fuses and gives out a white smoke, leaving some globules of metallic lead. When distilled it yields oxygen gas mixed with a little chlorine. The quantity of oxygen amounts to about one-fifth of the weight of the salt. Sulphuric acid and the alkalies throw down a white precipitate from the solution of this salt.\*

When chlorine is passed through water, having litharge diffused through it, a portion of the oxide is converted into peroxide of lead, and another portion into chloride of lead. No chlorate whatever is formed.

16. Carbonate of lead. Carbonic acid has no action whatever on lead, neither is it capable of dissolving its oxide; but it combines readily with the yellow oxide, and forms a carbonate. This salt is most easily obtained by precipitating lead from its solution in nitric acid by the alkaline carbonates. By that process it is obtained in the state of a white powder. It is tasteless and insoluble in water; but soluble in pure potash, in the same manner as the oxides of lead.

The white lead of commerce (or cerussa), employed as a paint, is merely a carbonate of lead, as Bergman first observed.† It is prepared by exposing thin plates of lead to the hot vapours of acetic acid. The metal is gradually corroded and converted into a carbonate, probably at the expense of the acid. The beauty of the colour depends principally on the purity of the lead employed.‡

This salt occurs native. In that state it is usually white, and has a good deal of lustre. Its specific gravity is 7.2357.§ It is often crystallized, and the primary form is a right rhombic prism, in which the faces are inclined to each other at angles of 117° 18′, and it usually occurs in prismatic modifications of this form. It is harder than calcareous spar, is translucent, and is distinguished by the diamond lustre. It is tasteless, and insoluble in water. When heated to redness it is decomposed,

<sup>\*</sup> Vauquelin; Ann. de Chim. xcv. 127.

<sup>†</sup> Opusc. i. 39. Proust showed the same thing. Jour. de Phys. lvi. 207. Scheele found that a little acetic acid was always separated from it when white lead was distilled with sulphuric acid. Crell's Annals, iii. 8. Eng. Trans.

<sup>‡</sup> The best English white lead is made at Newcastle-upon-Tyne. An account of the German process will be found in the Ann. de Chim. lxxii. 225.

<sup>§</sup> Bournon, Nicholson's Jour. iv. 220.

Class I. leaving protoxide of lead. The constituents of this salt are

1 atom carbonic acid . . . 2.75 · 1 atom protoxide of lead . . . 14

16.75

17. Phosphate of lead. This salt may be obtained by dropping phosphate of soda into a boiling-hot solution of chloride of lead, taking care that there is always an excess of chloride of lead present. It is a white heavy powder, tasteless, and insoluble in water; but soluble in nitric acid. It fuses easily before the blow-pipe, and on cooling crystallizes into a kind of irregular rhombic dodecahedron. When heated on charcoal it is partly reduced. Its constituents, when pure, are

1 atom phosphoric acid . . . 4.5 1 atom oxide of lead . . . 14

18.5

When nitrate of lead and phosphate of soda are mixed in the atomic proportions, the whole lead is precipitated, but a portion of the phosphoric acid remains in solution, so that the phosphate of lead obtained contains an excess of oxide of lead. For example, Berthier mixed together nitrate of lead and phosphate of ammonia, the phosphate of lead precipitated was found composed of

Phosphoric acid	•	•	77.5
Protoxide of lead	•	•	22.5

100

This is almost exactly

1	atom	phosphoric acid		4.5
11	atom	protoxide of lead	•	16.8

21.3\*

18. Sesquiphosphate of lead. Obtained by precipitating the hot solution of chloride of lead by means of biphosphate of soda, and washing the precipitate with hot water. It is a white insoluble powder which reddens litmus paper. Its constituents, according to the analysis of Berzelius, are

$l_{\alpha}^{1}$ atom phosphoric acid	•		6.75	Sect. XXIV.
1 atom protoxide of lead	•	•	14	

20.75

19. Biphosphate of lead. The preceding salts may be dissolved in aqueous phosphoric acid, and the solution when concentrated deposites granular crystals of biphosphate of lead.

20. Subsesquiphosphate of lead. This salt is obtained when the neutral phosphate is digested in ammonia, or when acetate of lead is precipitated by phosphate of soda. White and insoluble; not so easily melted as the phosphate. Before the blow-pipe on charcoal the excess of oxide is reduced, and phosphate of lead remains. Its constituents, according to the analysis of Berzelius, are

1 atom phosphoric acid . . 4.5  $1\frac{1}{0}$  atom oxide of lead . . 21

25.5

21. Phosphite of lead. This salt may be obtained by dissolving sesquichloride of phosphorus in water, saturating the solution with ammonia, and mixing it with chloride of lead dissolved in hot water. The precipitate is freed from all chloride of lead, by repeated washings in hot water. It is then to be pressed between folds of blotting paper, and dried in a vacuum over sulphuric acid. It is a white tasteless powder, insoluble in water. When heated it undergoes decomposition, water, phosphorus, and phosphurctted hydrogen gas being given out, and a subphosphate of lead remains. Its constituents, according to the analysis of Berzelius, are

1 atom phosphorous acid	•	•	3.5
1 atom protoxide of lead	•	•	14
1/2 atom water	•	•	0.5625

18.0625

22. Arseniate of lead. Arsenic acid attacks lead in a digesting heat, communicates a portion of its oxygen, and converts it into arseniate of lead in the state of an insoluble white powder. When arsenic acid is poured into the solution of lead in nitric, muriatic, or arsenic acids, arseniate of lead precipitates in powder. The salt may be formed by decomposing nitrate of lead with arseniate of soda, taking care not to add an excess of the last salt. It is a white tasteless powder, insoluble in

water and acetic acid, but soluble in nitric and muriatic acids.

Easily fusible by heat. Its constituents are

21.25

23. Subsesquiarseniate of lead. Obtained by precipitating acetate of lead by means of arseniate of soda, and by digesting arseniate of lead in ammonia. It is a white fusible powder, composed, according to the analysis of Berzelius, of

24. Arsenite of lead. Precipitate acetate of lead by ammonia, and saturate the precipitate with arsenious acid. A white powder, which fuses, when heated, into a very electric glass globule. Its constituents, according to the analysis of Berzelius, are

1 atom arsenious acid . 6.25 1 atom protoxide of lead . 14

20.25

25. Binarsenite of lead. Obtained by digesting hydrous protoxide of lead with arsenious acid. A white powder. When rubbed in a mortar, it becomes as electric as sulphur. When heated, it melts with the evolution of water, and some arsenious acid, into a yellow, ideo-electric glass. It is slightly soluble in water. Its constituents, according to the analysis of Berzelius, are

2 atoms arsenious acid . 12.5 1 atom protoxide of lead . 14

26.5

26. Borate of lead. Boracic acid has no action on lead; but borate of lead is precipitated in the state of a white powder when borate of soda is mixed with nitrate of lead. Before the blow-pipe it melts into a colourless glass.\* When one part of boracic acid is melted with two parts of red oxide of lead, the product, according to Reuss, is a greenish-yellow, transparent, hard, insoluble glass.†

<sup>\*</sup> Wenzel's Verwandt, p. 252.

27. Silicate of lead. Silica and protoxide of lead melt when beated into a yellow glass.

28. Selenite of lead. This salt has the form of a heavy white powder, which falls very rapidly, and which is not soluble in an excess of acid. When heated, it melts and becomes transparent and yellow. On cooling it recovers its white colour, becomes opaque, and exhibits a crystalline texture. In a heat nearly white it boils, and selenic acid sublimes, and there remains a subselenite, which is semitransparent and friable, and has a strongly marked crystalline texture. The selenite of lead, according to the analysis of Berzelius, is composed of

- 29. Antimoniate of lead. This salt is obtained by pouring antimoniate of potash into nitrate of lead. It precipitates in the state of a white matter, very similar in appearance to chloride of lead. It is quite insoluble in water. Before the blow-pipe on charcoal it is reduced to the metallic state, constituting an alloy of antimony and lead. Nitric acid does not decompose it completely; so that Berzelius, to whom we are indebted for every thing known respecting the antimoniates, was unable to analyze it.+
- 30. Antimonite of lead. This salt may be obtained by the same process as the preceding, which it perfectly resembles in its properties.
- 31. Tellurate of lead is a whitish powder. When heated it loses its water of combination, and becomes yellow. In a little higher temperature it fuses and forms a semitransparent mass similar to chloride of lead. It is obviously a bitelluret, composed of

32. Chromate of lead. Formed by mixing chromate of potash and nitrate of lead. It is a splendid orange powder, tasteless, and insoluble in water, but soluble in nitric acid. It

<sup>\*</sup> Ann. de Chim. et de Phys. ix. 339.

<sup>+</sup> Berzelius, Nicholson's Jour. xxxv. 41.

<sup>‡</sup> Ibid. xxxv. 45.

Class I.

occurs native, of a scarlet colour, and crystallized in oblique rhombic prisms. The faces of the prism make angles with each other of 93° 30′. The base of the prism is inclined to the lateral faces at an angle of 99° 10′. It is anhydrous, and composed of

1 atom chromic acid . . 6.5 1 atom protoxide of lead . 14

20.5

33. Dichromate of lead. This salt was first pointed out by Dulong in 1812, and afterwards by Grouvelle in 1822. It is easily obtained by digesting chromate of lead in caustic potash. It is a powder of a fine scarlet colour, and insoluble in water. When ignited, its colour becomes brick-red; but the original colour is again restored when it cools. When digested in nitric acid, it is again converted into common chromate. The nature of this salt was shown by Mr. Badams in 1825.\* It is anhydrous, and composed of

1 atom chromic acid . . 6.5 2 atoms protoxide of lead . 28

34.5

34. Molybdate of lead. This salt is precipitated in a light yellow powder, when solutions of molybdate of ammonia and nitrate of lead are mixed together. It occurs native in Carinthia. Its composition was first detected by Klaproth. It has a yellow colour, and is completely insoluble in water. Its specific gravity is 5.706.† Its crystals are cubic or rhomboidal plates. The primary form of its crystals is an octahedron, with a square base. When heated, it decrepitates and melts into a yellowish mass. It is soluble in fixed alkalies and in nitric acid. Muriatic acid decomposes it by the assistance of heat, and carries off the lead. It is anhydrous, and composed of

35. Tungstate of lead. This salt occurs native, crystallized in right prisms with square bases. It is yellowish. Insoluble

<sup>\*</sup> Annals of Philosophy (2d series), ix. 303.

<sup>†</sup> Hatchett, Phil. Trans. 1796.

in water, harder than gypsum, has a specific gravity of 8, a seet. XXIV. brownish-white colour, and translucent. Its constituents, according to the analysis of Lampadius, are

Tungstic acid Protoxide of lead	•	•	51·75 48·25
			100

This is obviously

lously	
1 atom tungstic acid	15.5
1 atom protoxide of lead .	14
_	29.5

36. Bitungstate of lead. Obtained by precipitating nitrate of lead with tungstate of ammonia. It is a white powder, insoluble in water. Its constituents, according to the analysis of Berzelius, are

	Tungstic acid	•		71.42
•	Protoxide of lead	•	•	28.58
771 ·				100
This approac	_			
2	2 atoms tungstic ac	id		31
]	atom protoxide of	f lead	•	14
				45

There is a slight deficiency in the lead, provided our number for the atomic weight of tungstic acid be correct.

- 37. Uraniate of lead. It may be obtained by mixing together solutions of nitrate of lead and nitrated peroxide of uranium, and precipitating by ammonia. The yellow precipitate is insoluble in water, and when heated to redness, becomes cinnamon brown.\*
- 38. Oxalate of lead. Lead is precipitated from all its solutions by oxalic acid. This salt is best obtained by mixing oxalate of ammonia and nitrate of lead together in the atomic proportions. It is a white, tasteless powder, insoluble in water and acetic acid; but soluble in the stronger acids, and somewhat soluble even in oxalic acid. When heated sufficiently, it is converted into oxide of lead, mixed with a little metallic lead. Its constituents are

Class f.

1 atom oxalic acid . . 4.5
1 atom protoxide of lead . 14

٠,

18.5

39. Acetate of lead. This salt has been long known. It is mentioned by Isaac Hollandus and Raymond Lully. It received formerly a great variety of names; such as, sugar of lead, sugar of Saturn, salt of Saturn, &c.

This salt is employed in considerable quantities by dyers and calico-printers. They mix it with alum or with sulphate of iron, and by that means compose acetate of alumina or of iron, according to the process; salts which answer much better as mordants for fixing their colours than alum or green vitriol. It is prepared in considerable quantities both in this country and in Holland and France. The manufacturers distil their own acid in England and Holland from sour beer, and in France from sour wine. The different processes followed by manufacturers have been described by Weber\* and Demachy,† and more lately by Pontier.‡ Of late the acid is obtained from wood.

These processes may be reduced to two; either lead in the metallic state is exposed to the action of the acetic acid, or the carbonate of lead is dissolved in it. In the first case, thin plates of lead are put into earthen vessels along with acetic acid. The portion of the lead near the surface, as soon as it is covered with a coat of oxide, is removed to the bottom of the vessel, and new plates are brought to the surface. These are incrusted in their turn, and removed to the bottom, where the oxide is dissolved. This change of place is continued daily till the acid has dissolved a sufficient quantity of lead. It is then filtered, and sufficiently concentrated by evaporation. As it cools, the acetate of lead precipitates in small crystals.

Other manufacturers dissolve the carbonate of lead, prepared by exposing the metal to the fumes of vinegar; or they make use of litharge in its stead, and the solution is evaporated in the usual way till the salt crystallizes. This process is considered as more expensive than the other: but might not native

<sup>\*</sup> Phys. Chem. Magazin. i. 84.

<sup>†</sup> Laborant in grossen, ii. 194.

<sup>†</sup> Ann. de Chim. xxxvii. 268.

carbonate of lead, which is found abundantly in many places, be employed with advantage in- < stead of these artificial oxides?



The crystalline form is a right oblique angled prism, usually modified as in the margin. The following are the measurements of Mr. Brooke,\* which in general agree within a few minutes of my own:

d on d'	•	•	128°	O'
d on M	•	•	116	0
d on T	•	•	98	<b>30</b>
M on T	•	•	109	32

Its taste is sweet and somewhat astringent. Its specific gravity is 2.575. When water is boiled upon this salt, it dissolves about .29, and retains in solution when cold about .27 of its weight of it.† When exposed to the air, it undergoes no change. Its constituents are easily separated. When it is dissolved in water, a small quantity of white powder usually falls. It is carbonate of lead, formed by the carbonic acid, which usually exists in water. When we blow through a solution of acetate of lead, the same white powder precipitates.‡ 200 gr. of alcohol of 0.835 dissolve 15.7 gr. of acetate of lead at 60°.

This salt is decomposed by all those acids and their compounds which form with lead a salt nearly insoluble in water; as the sulphuric, phosphoric, muriatic, fluoric, oxalic, malic, &c. When heated, it is decomposed; and if it be distilled in a retort, very singular products are obtained. These products were first examined by Beccher; afterwards by Baumé, and more particularly by Pluvinet: but it is to Proust that we are indebted for the most precise information on the subject. By distilling 160 parts of sugar of lead, he obtained by a gentle heat 12 parts of water slightly acidulated with vinegar. Then by increasing the fire, there came over 72 parts of a yellow liquid, having the odour of alcohol, strong and agreeable, though mixed with an empyreumatic smell. When lime is added to the liquid, ammonia is disengaged, which existed in the liquid, combined with a slight excess of acetic acid. When

<sup>\*</sup> Annals of Philosophy (2d series), vi. 374.

<sup>†</sup> Bostock, Nicholson's Jour. xi. 79. Wenzel affirms, that water at the temperature of 100° dissolves its own weight of this salt. Verwandtschaft, p. 308. But this is a mistake.

<sup>‡</sup> Proust, Jour. de Phys. lvi. 207.

Close T.

the liquid was saturated with potash, and allowed to remain for 24 hours, about one-third of a part of oil separated and floated on its surface. This oil being separated by a syphon, was found to have a strong odour. The liquid was then distilled by means of a low heat. The first eight parts which came over were of the specific gravity 0.88. This liquid mixed with water exactly like alcohol. Its taste was strong, and its volatility scarcely inferior to that of ether. It burns rapidly, and with a large white flame, when brought near a lighted candle. It contained manifestly a considerable portion of water.\* During the distillation abundance of carbonic acid gas is disengaged, but no sensible portion of any other elastic fluid. The constituents of acctate of lead are

1 atom acetic acid		6.25
1 atom protoxide of lead		14.00
3 atoms water	•	3.375
		23:625

40. Diacetate of lead. This salt may be obtained by boiling a solution of acetate of lead over litharge, added in the atomic proportions. The litharge is dissolved, and by evaporating the solution, the diacetate is deposited in the state of a beautiful white sediment, having a crystalline aspect, though the form cannot be determined. It has a sweet and astringent taste, and is soluble in water. Its constituents are

1 atom acetic acid .	•	6.25
2 atoms protoxide of lead	•	28
10 atoms water .	•	11.25

41. Trisacetate of lead. This salt was first obtained by Thenard by boiling 23.625 parts of crystallized acetate of lead, and 35.44 parts of litharge. The liquid deposites the salt in white plates. It is soluble in water; but less so, and has a less sweet taste than acetate of lead. Its constituents, according to the analysis of Berzelius, are

1 atom acetic acid .	•	6.25
3 atoms protoxide of lead	•	42
		40.05

According to Thenard's analysis, it contains also 2 atoms of water.

<sup>\*</sup> Proust, Jour. de Phys. lvi. 209.

The solution of the oxide of lead in acetic acid was strenu- sect. XXIV. ously recommended by Goulard, a surgeon in Montpelier, as an excellent application in cases of inflammation. It was prepared by boiling distilled vinegar on litharge till it refused to dissolve any more of the oxide. This preparation was distinguished by the names of Goulard's extract and vinegar of lead. Scheele first ascertained the nature of this substance, by showing that solution of sugar of lead in water is converted into Goulard's extract, by keeping in it a plate of lead for the space of a day; and by proving that the solution oxidized and dissolved a portion of the plate.\* But subsequent writers had overlooked the observations of this chemist, till Dr. Bostock examined Goulard's extract, and by comparing it with sugar of lead, showed that it is in reality a solution of subacetate of lead in water.+ It is precipitated in much greater proportion by carbonic acid than the acetate; and it is a much more delicate test for mucilage or gum, as was known to chemists long before Mr. John Hunter employed it as a reagent.

42. Hexacetate of lead. This salt may be obtained by boiling in water a mixture of one part of acetate of lead, and two parts of litharge; or by decomposing acetate of lead by a considerable excess of ammonia. It is a white powder, slightly soluble in boiling water, but deposited in feather-shaped crystals when the solution cools. Its constituents, according to the analysis of Berzelius, are

1 atom acetic acid 6.256 atoms protoxide of lead 3 atoms water 3.375

93·625±

43. Lactate of lead. It is obtained by digesting an alcoholic solution of lactic acid on finely powdered litharge, till the liquid acquires a sweet taste. The liquid being then evaporated to the consistence of honey, deposites the lactate in small grains, which may be purified by washing them in alcohol. When dry, they are light and silvery. They are not

\* Crell's Annals, iii. 10. Eng. Trans. + Nicholson's Jour. xi. 75. † The result of the analysis was: Acetic acid Protoxide of lead 91:3 Water 3.0

changed in the air. When treated with sulphuretted hydrogen, pure lactic acid may be obtained.

44. Bilactate of lead. When lactic acid is digested on car-

- 44. Bilactate of lead. When lactic acid is digested on carbonate of lead it becomes browner than before; but cannot be fully saturated by the oxide. We obtain an acid salt which does not crystallize, but dries into a syrup like brown mass, with a sweet austere taste.
- 45. Sublactate of lead. If we digest lactic acid on a greater proportion of litharge than is necessary for its saturation, the liquid acquires at first a browner colour; but, as the digestion proceeds, the colour becomes lighter, and the oxide swells into a bulky powder. If the whole be evaporated to dryness, boiled in water, and the liquid filtered while hot, it deposites on cooling a light yellow powder, which is sublactate of lead. When dried it is mealy and soft to the touch. It is decomposed by the weakest acids. When warmed and set on fire at one point it burns like tinder, and leaves the lead in a great measure reduced. According to the experiments of Berzelius, this salt is composed of

Acid	•	•	•	17
Oxide o	of lead	•	•	83
			41	
				100

But he considers the proportion of lead thus stated as too high.\*

46. Formate of lead. When litharge is dissolved in formic acid to saturation, a white salt in crystals, resembling acetate of lead, is obtained. Its taste is sweet and astringent. It decrepitates when heated, then melts, and is decomposed. Its constituents, according to the analysis of Göbel, are

1 atom	formic acid	i	•	•	4.625
1 atom	protoxide o	of lea	d	•	14
1 atom	water	•	•	•	1.125
					10.75

47. Mellate of lead. When mellate of ammonia is mixed with a solution of nitrate of lead, a white bulky precipitate falls, which gradually contracts into a heavy powder, not soluble in water, but soluble in nitric acid. It is composed, according to the analysis of Walchner, of

<sup>\*</sup> Berzelius, Djurkemien, ii. 439.

Mellitic acid . . . . 32.95
Protoxide of lead . . . . 67.05

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#### 100\*

48. Tartrate of lead. Tartrate of potash, when mixed with nitrate of lead in the atomic proportion, lets fall a white powder, which is tartrate of lead. It is a tasteless powder, insoluble in water, but soluble in tartaric acid. It is anhydrous, and composed of

1 atom tartaric acid . 8.25
1 atom protoxide of lead . 14
22.25

49. Vinate of lead. Vinate of soda precipitates this salt from acetate of lead. It is in flocks consisting of soft needles, soluble in an excess of vinic acid, and composed, according to Walchner, after being dried in the temperature of 223°, of

### 100

- 50. Pyrotartrate of lead. When pyrotartrate of potash is mixed with acetate of lead, after an interval of some hours a crystallized salt is deposited in hemispherical concretions.
- 51. Citrate of lead. Citric acid does not attack lead, but when dropped into acetate of lead a citrate precipitates in the state of a difficultly soluble powder.‡ The constituents of this salt are

52. Pyrocitrate of lead. When pyrocitrate of potash is dropped into acetate of lead, a white, translucent, gelatinous precipitate falls, which diminishes much on drying, contains 8 per cent. of water, and (abstracting the water) is a compound of

<sup>\*</sup> Poggendorf's Annalen, vii. 333.

<sup>§</sup> Lassaigne, Ann. de Chim. et de Phys. xxi. 105.

Class 1.

- 53. Malate of lead. Malic acid does not attack lead, but when poured into a solution of lead in nitric or acetic acid, malate of lead is immediately precipitated;\* and likewise, as Vauquelin has observed, when acetate of lead is poured into a solution containing acetate of lime. This precipitate is easily distinguished by the form of fine light flakes which it has, and by the facility with which it is dissolved by the acetic and weak nitric acids.† We learn from the experiments of Mr. Donovan, that there are three subspecies of this salt.
- 1. The neutral malate. If obtained by precipitation it is a white powder, but if obtained from solution in its own acid it is in beautiful silvery crystals. It is quite insoluble in water.
- 2. Submalate. A white insoluble matter. If in mass, it is dense and hard; if in powder, it is gritty.
- 3. Supermalate. This salt never assumes the solid form. It has a sweet taste.
- 54. Pyromalate of lead. When pyromalate of potash is dropped into acetate of lead white flocks fall down, which gradually assume the form of a translucent jelly. When washed on the filter it diminishes in size, and assumes the form of small needles having a pearly lustre.§
- 55. Fungate of lead. Fungate of potash precipitates acetate of lead in a state similar to chloride of silver. The precipitate dissolves readily in acetic acid.
- 56. Mucate of lead. Mucate of potash throws down a white precipitate from nitrate of lead. This salt is insoluble in water. It is composed of

1 ato	m muc	ic acid	•	•	13
1 ato	m prote	oxide of	lead	•	14
	•				

- 57. Pyromucate of lead. Pyromucic acid digested in protoxide of lead forms a neutral solution, which, when concentrated, furnishes brown, translucent, oily-looking drops, and the whole liquid gradually assumes that form. On cooling it gradually concretes into a solid white mass.¶
- 58. Succinate of lead. Succinic acid scarcely attacks lead, but it dissolves its yellow oxide; and the solution according to
  - \* Scheele, Crell's Annals, ii. 7. Eng. Trans.
  - † Ann. de Chim. xxxv. 155. † Donovan, Phil. Trans. 1815.
  - § Lassaigne, Ann. de Chim. et de Phys. xi. 53.
  - Braconnot. ¶ Labillardiere.

Wenzel, yields long slender foliated crystals,\* scarcely soluble sect. XXIV. in water, but soluble in nitric acid. Succinic acid does not precipitate lead from nitric or muriatic acid, but it occasions a precipitate in acetate of lead.† The constituents of this salt, according to the analysis of Berzelius,‡ are as follows:

1 atom succinic acid . . 6.25 1 atom protoxide of lead . 14 20.25

59. Trissuccinate of lead. By digesting the neutral succinate in ammonia, Berzelius obtained a subsuccinate composed of 1 atom acid + 3 atoms oxide of lead. Its constituents were

100.00

60. Benzoate of lead. Benzoic acid dissolves lead with difficulty. The solution yields by evaporation crystals of benzoate of lead of a brilliant white colour, soluble in alcohol and water, not altered by exposure to the air, but decomposed by heat, which drives off their acid. The sulphuric and muriatic acids separate the lead.§ This salt is composed as follows:

61. Trisbenzoate of lead. Berzelius obtained this salt by digesting the neutral benzoate in caustic ammonia. A white anhydrous powder. He found it composed of 1 atom acid + 3 atoms oxide of lead, or by weight of

100

62. Gallate of lead. When gallate of ammonia and nitrate of lead are mixed at a boiling temperature a grayish-white.

<sup>\*</sup> Wenzel's Verwand. p. 241.

<sup>†</sup> Stockar de Neuforn de Succino, § 33, as quoted by Gren, Handbuch, iii. 281.

Annals of Philosophy, v. 181.

powder falls, which is gallate of lead. Its constituents, according to the analysis of Berzelius, are

63. Trisgallate of lead. When the preceding salt is digested with an aqueous solution of ammonia it is converted into a trisgallate, composed, according to Berzelius, of

64. Kinate of lead. It may be obtained by digesting carbonate of lead in kinic acid. It forms irregular crystals.\*

65. Subkinate of lead. This salt precipitates when solutions of kinate of lime and Goulard's extract are mixed together.

66. Meconate of lead. Meconate of soda precipitates acetate of lead in white heavy flocks.+

67. Boletate of lead. Boletate of potash throws down a white precipitate from nitrate of lead.

68. Camphorate of lead. Camphorate of potash throws this salt down when mixed with nitrate of lead. It is a white powder, insoluble in water. It is composed, according to Brandes, of

# 100.000§

- 69. Suberate of lead. Suberate of ammonia when mixed with nitrate of lead throws down a heavy white curdy precipitate, which dries into a white powder having a weak sweetish taste, not soluble in water, but soluble in weak acetic acid.
- 70. Stearate of lead. It is obtained by mixing together boiling solutions of nitrate of lead and stearate of potash. The precipitate must be washed till the water employed is not coloured by sulphuretted hydrogen gas. It is white, fusible, and without smell.
- 71. Substearate of lead. It is prepared in the same way, by employing subacetate of lead instead of the nitrate. It is

<sup>\*</sup> Henry and Plisson. † Sartürner. ‡ Braconnot.

<sup>§</sup> Schweigger's Jour. xxxviii. 298. || Chevreul, sur les corps gras, p. 55.

colourless, and very fusible. After fusion it is transparent and sect. XXIV. may be pulverized by trituration.\*

- 72. Margarate of lead.
  73. Submargarate of lead.

  They may be prepared in the same way as the two preceding salts, which they resemble in their properties.
- 74. Suboleate of lead. It may be obtained by boiling an excess of subacetate of lead with oleic acid. This salt, almost liquid at 212°, is transparent after having been melted. At the temperature of 68°, it is soft.‡
- 75. Phocenate of lead. Phocenic acid readily dissolves protoxide of lead. By evaporation we obtain the salt in beautiful transparent plates, which are ductile.
- 76. Trisphocenate of lead. When phocenic acid is heated with dry massicot a combination is produced. When cold water is digested in it we obtain a solution, which, when evaporated, yields crystals in small brilliant needles grouped in hemispherical masses. These crystals constitute a trisphocenate of lead. This salt has a weak taste of phocenic acid, is not very soluble in water, absorbs carbonic acid from the air, and is not fusible.
- 77. Butyrate of lead. It may be obtained by dissolving protoxide of lead in butyric acid. When the solution is evaporated it deposites very fine silky needles.¶
- 78. Trisbutyrate of lead. It may be obtained by the same process as the subphocenate. It does melt. Its taste is slight, and it is not very soluble in water. The solution absorbs rapidly carbonic acid from the air.\*\*
- 79. Cholesterate of lead. Obtained by double decomposition. At first tile-red, but when dried assumes a dirty red colour. It is composed of

### 100.00++

80. Pinate of lead. It may be obtained by various processes, one of the easiest of which is to mix alcoholic solutions of acetate of lead and pinic acid. A white soft powder, not cohering at 212°. At a higher temperature it fuses into a translucent resin without decomposition. It is composed of about

<sup>\*</sup> Chevreul, sur les corps gras, p. 56. † Ibid. p. 69. ‡ Ibid. p. 97.

<sup>§</sup> Ibid. p. 112. || Ibid. p. 113. || Ibid. p. 128. \*\* Ibid. p. 129.

<sup>††</sup> Pelletier and Caventou.

Class I.

Protoxide of lead . . . 100

19.5

119.5

It is insoluble in water, very little soluble in alcohol and ether, but dissolves readily in oil of turpentine and the fat oils.\*

81. Indigotate of lead. The indigotic acid does not seem inclined to form neutral combinations with protoxide of lead. At least the attempts of M. Buff to form a neutral indigotate of lead were unsuccessful.

When carbonate of lead mixed with water is added by small portions at a time to a boiling solution of indigotic acid, the solution, after being filtered and allowed to cool, deposites indistinct crystals of a pale yellow colour, and composed of

Indigotic acid . . 100
Protoxide of lead . . 57.3

If we dissolve a little carbonate of lead in a great deal of indigotic acid the liquid on cooling deposites semitransparent yellow needles, which may be freed from adhering acid by washing them in alcohol. They are anhydrous, dissolve readily in water, but are at the same time partially decomposed. These crystals are composed of

Indigotic acid . . . 100
Protoxide of lead . . . 52·4

When a little nitrate of lead is poured into a boiling solution of indigotate of potash the liquid remains for a little transparent, but it gradually deposites a great number of very fine needles, having a deep yellow colour. This salt is completely insoluble in water, and is a compound of

Indigotic acid . . 100
Protoxide of lead . . 103.4

The salt obtained is quite different when indigotate of potash is poured into a hot solution of nitrate of lead, a very bulky crystalline precipitate falls, of a pale-yellow colour, which becomes deeper on cooling. It is very soluble in hot water, and insoluble also in cold water. It is composed of

Indigotic acid . . 100
Protoxide of lead . . 59.7

When this salt is heated with liquid ammonia a deep-yellow powder is obtained, very fine, and quite insoluble in water. It is composed of Indigotic acid . . 100
Protoxide of lead . . 128\*

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82. Pyrurate of lead. When pyrurate of soda and sub-acetate of lead are mixed a subpyrurate of lead is obtained, composed of

100 +

- 83. Nitrosaccharate of lead. A matter resembling gum, uncrystallizable, and not altered by exposure to the air. When heated it produces a kind of explosion.
- 84. Allentoate of lead. It is soluble and crystallizable. It has a sweetish and styptic taste, and is composed of

Allentoic acid	•	•	80.65
Protoxide of lead			19.35

## 100 §

- 85. Sulphovinate of lead. It may be obtained by saturating the residuum after the preparation of ether with carbonate of lead. It does not crystallize but forms a white matter, which absorbs moisture from the atmosphere and speedily runs into a liquid. When distilled it furnishes a white oil which sinks in water, then a liquid smelling of ether, sulphurous acid, sulphuric acid, and sulphate of lead remains. This salt dissolves in less than half its weight of water, and is also very soluble in alcohol.
- 86. Sulphonaphthalate of lead. This salt is white, solid, crystalline, and soluble in water and alcohol. It has a bitter metallic taste, with very little sweetness.
- 87. Vegetosulphate of lead. A very soluble salt having a gummy appearance.\*\*
- 88. Sinapate of lead. Sinapic acid precipitates subacetate. of lead white.++
  - \* Ann. de Chim. et de Phys. xli. 179.
  - † Chevallier and Lassaigne, Ann. de Chim. et de Phys. xiii. 161.
  - † Braconnot, ibid. p. 116. 
    \$ Lassaigne, ibid. xvii. 302.
  - || Vogel, Gilbert's Annalen, lxiii. 93.
  - ¶ Faraday, Annals of Philosophy (2d series), xii. 210.
  - \*\* Braconnot, Ann. de Chim. et de Phys. xii. 186.
  - †† Henry and Garot.

#### SECTION XXV. - SALTS OF PROTOXIDE OF TIN.

Though several of the salts of tin are of great importance in the art of dyeing, and have been known to manufacturers ever since the discovery of the scarlet dye, of which the oxide of tin constitutes a necessary ingredient, it is only of late that the nature and constitution of these salts have been examined with any kind of precision, and that a satisfactory explanation has been given of the curious properties which some of them possess, and the great changes to which they are liable. For the progress which this branch of the science has made, we are chiefly indebted to Adet, Pelletier, and Proust.

Tin, like iron, combines with two doses of oxygen, and forms two distinct oxides, with each of which several of the acids are capable of combining; and those salts which contain the metal oxidized to a minimum are extremely ready to absorb oxygen, and to pass into the state of oxygenized salts. The salts of tin may be distinguished by the following properties:

The protoxide has by far the strongest affinity for acids, though its affinity is weaker than that of the greater number of bases.

Characters.

- 1. The protosalts of tin are white, and the solutions of them are usually colourless. Their taste is astringent and metallic, being highly disagreeable. When in solution they rapidly absorb oxygen, and are converted into the corresponding per salts.
- 2. When a plate of zinc or lead is put into a solution of tin that metal is thrown down in the metallic state.
- 3. Prussiate of potash occasions a white gelatinous precipitate when dropped into these solutions.
- 4. Hydrosulphuret of potash occasions a coffee-brown precipitate in the salts containing the protoxide of tin.
- 5. Neither gallic acid nor the infusion of nutgalls occasion any precipitate.
- 6. When muriate of gold is poured into solutions containing tin combined with a minimum of oxygen, a purple-coloured precipitate falls.
- 7. A solution of potash throws down a white precipitate, which dissolves in an excess of the alkali. If the solution be boiled a black powder falls, which is metallic tin; while a compound of peroxide of tin and potash remains in solution.

- 8. Ammonia throws down a white precipitate, not soluble sect. xxv. in an excess of ammonia.
  - 9. The solutions of protoxide of tin redden litmus paper.
- 1. Sulphate of tin. When solutions of protochloride of tin and sulphate of soda are mixed in atomic proportions, no change takes place at first. But, on concentrating the solution, small globular masses were deposited. They consisted of a congeries of small needles diverging from a centre. The taste of this salt is astringent and sour, it reddens vegetable blues, and is soluble in water.

This salt was described imperfectly by Monnet many years ago. He obtained it crystallized in needles. The simplest method of obtaining it is that which was pointed out by Berthollet, junior. Pour sulphuric acid into protochloride of tin; a white powder falls, which is the sulphate. It dissolves in water, and forms by evaporation small prismatic crystals. Alkalies decompose it imperfectly, throwing down a subsulphate of tin.\*

When it is exposed to a red heat, sulphurous acid and oxygen gas are given off and peroxide of tin remains.

- 2. Sulphite of tin. The action of sulphurous acid upon tin was examined by Fourcroy and Vauquelin, during their experiments on the combinations which that acid is capable of forming. When a plate of tin is plunged into liquid sulphurous acid, it assumes a yellow colour, and afterwards becomes black. A black powder is precipitated, which is sulphuret of tin. A portion of the acid is decomposed; the tin is partly oxidized, and combined with the remainder of the acid, and partly precipitated in the state of sulphuret combined with the sulphur of the decomposed acid. There remains in solution hyposulphite of tin; for sulphur precipitates when sulphuric acid is added to the solution.†
- 3. Hyposulphite of tin. Muriate of tin occasions no precipitate in the solution of an alkaline hyposulphite. Hence the hyposulphite of tin must be a soluble salt. ‡
- 4. Nitrate of tin. Nitric acid acts with amazing energy upon tin, and converts it into an oxide with the evolution of a great deal of heat; but there seems to be but a very feeble affinity between that acid and the oxides of tin. Hence the union which they form is but of transient duration, the oxides separating when any attempt is made to concentrate the solu-

<sup>\*</sup> Statique Chimique, ii. 464. † Fourcroy, vi. 30. † Herschell, Edin. Phil. Jour. i. 24.

Class I.

tion. This has been long known to chemists, and has occasioned a variety of attempts to make the solution of tin in nitric acid more permanent; but these attempts, as might have been expected, have not been attended with success.

When nitric acid of the specific gravity 1.114 is poured upon tin, the metal is dissolved rapidly with effervescence and a great elevation of temperature, which ought to be moderated by plunging the vessel containing the mixture in cold water. In this case the oxygen is chiefly furnished by the water, and the tin is only combined with a minimum of oxygen. solution, therefore, which is of a yellow colour, is a real nitrate It becomes gradually opaque, and deposites a white powder, which is an oxide of tin, with a minimum of oxygen, as Proust has demonstrated. This oxide separates in great abundance if the solution be heated. During the solution of the tin a quantity of ammonia is formed. When potash is dropped into the liquid, this ammonia becomes sensible by its odour. Hence, we see that, during the solution, both water and nitric acid have been decomposed; their oxygen combined with the tin, and the hydrogen of the one uniting with the azote of the other, formed ammonia. If a little nitric acid be poured in and heat applied, the tin precipitates in the state of a peroxide.\*

The easiest way of obtaining the nitrate of tin is to dissolve the hydrated protoxide of tin in dilute nitric acid. It is a yellow-coloured solution, which cannot be concentrated, or even kept, without the tin gradually being peroxidized. The consequence is that the properties of this salt cannot be studied.

- 5. Carbonate of tin. As far as is known at present, the oxides of tin do not combine with carbonic acid. Bergman failed in his endeavours to form this combination; and when the oxides of tin are precipitated from their solution in acids by alkaline carbonates, he found that their weight receives scarcely a perceptible increase. † Nor have the attempts of Proust to combine these bodies with carbonic acid been attended with more success. ‡
- 6. Phosphate of tin. Phosphoric acid has scarcely any action on tin unless when it is exposed dry and mixed with that metal to the action of a strong heat. In that case, part of the acid is decomposed, its phosphorus combines with one portion of the tin and forms a phosphuret, while the oxide of

<sup>\*</sup> Proust, Jour. de Phys. li. 173.

<sup>†</sup> Opusc. ii. 329:

<sup>‡</sup> Jour. de Phys. li. 167.

tin unites with the undecomposed acid and forms a phosphate. \* Sect. XXV. This salt precipitates also when the alkaline phosphates are mixed with a solution of protochloride of tin; and it may be formed by digesting oxide of tin in phosphoric acid. It is a white powder, insoluble in water. Tin does not precipitate copper from muriatic acid. Phosphate of tin melts into a glass when heated. +

7. Phosphite of tin. This salt may be obtained by mixing together solutions of protochloride of tin and protochloride of phosphorus saturated with ammonia. It is a white insoluble powder. When dissolved in muriatic acid it constitutes a powerful reactive for the difficultly oxidable metals. When heated it swells up, becomes black, and melts without any luminous appearance. It yields a gas which contains a good deal of phosphorus, and phosphorus even sublimes from it. Its constituents appear to be

1 atom phosphorous acid . . . 3.51 atom protoxide of tin . . 8.25  $\frac{1}{2}$  atom water . . . 0.5625

12.3125‡

- 8. Arseniate of tin. When tin is treated with arsenic acid in a digesting heat, it is slowly oxidized at the expense of the acid, and the solution at last assumes the form of a gelatinous mass. Arsenic acid precipitates tin from acetic acid, and the alkaline arseniates occasion a precipitate when poured into protochloride of tin. The precipitate is arseniate of tin in the form of an insoluble powder, which hitherto has not been examined.§
- 9. Borate of tin. Boracic acid does not attack tin; but borax produces a precipitate in the protochloride of tin. The white powder which falls is insoluble in water: in a strong heat it melts into an opaque slag.
- 10. Chromate of tin. When protochloride of tin is mixed with an excess of chromate of potash, dense brownish-yellow flocks precipitate. When we dissolve them in muriatic acid the salt is destroyed, the chromic acid being converted into green oxide and the tin into peroxide.
- 11. Oxalate of tin. Oxalic acid attacks tin when assisted by heat. The metal is first blackened, and is then covered

<sup>\*</sup> Pelletier, Ann. de Chim. xiii. 16. † Wenzel's Verwandtchaft, p. 175. † Mitcherlich, Ann. de Chim. et de Phys. xxxv. 218. § Scheele, i. 180 | Wenzel's Verwandtschaft, p. 252.

Class I.

with a white crust of oxide. The solution, which has an austere taste, by slow evaporation yields prismatic crystals; but when evaporated rapidly by means of a strong heat, it leaves a mass resembling horn. \*

12. Croconate of tin. Croconate of potash, when dropped into protochloride of tin, throws down a white precipitate. †

13. Acetate of tin. Acetic acid attacks tin very slowly, even when assisted by heat, and oxidizes and dissolves only a small portion of it. The spontaneous action of this acid on tin vessels, when in the state of vinegar, was examined by Vauquelin. The subject was of importance, because vinegar is usually measured out in tin vessels. Now, as these vessels contain always a little lead, and as the salts of lead are all poisonous, it was of consequence to determine whether the vinegar acted on the vessel, and if it did, whether its action was confined to the tin, or extended also to the lead; because in this last case the vinegar would be converted into a poison. The result of this investigation was, that a small portion of tin was dissolved; and that when the lead exceeded the sixth part of the tin, a small portion of it was also dissolved at that part of the vessel only which was in contact both with the vinegar and the air. 1

When acetic acid is boiled upon tin, the metal is gradually dissolved, combining with oxygen at the expense of the water. The solution has a whitish colour, and yields by evaporation small crystals. This fact, first mentioned by Lemery, had been denied by Monnet, Westendorf, and Wenzel, who could only obtain from it a gummy mass. But Morveau established the truth of Lemery's observation, by crystallizing acetate of tin by spontaneous evaporation. § It is easy to account for the different results obtained by these chemists. The crystals were, no doubt, acetate of tin, the gummy mass peracetate of tin. The simplest method of obtaining the acetate of tin is to mix together the solutions of protochloride of tin and acetate of lead.

- 14. Lactate of tin. The solution of tin in lactic acid when concentrated lets fall some peroxide of tin, and deposites small octahedral crystals of lactate of tin.
- 15. Formate of tin. A white insoluble powder, becoming black when heated.
  - 16. Tartrate of tin. A solution of tartaric acid readily
  - \* Bergman, i. 269. + L. Gmelin. + Ann. de Chim. xxxii 243.
  - § Encycl. Method. Chim. i. 23. | Braconnot. ¶ Arfvedson.

dissolves tin, and tartrate of tin is gradually deposited in Sect. XXVI. needles not easily soluble in water.

- 17. Vinate of tin. Tin dissolves very slowly in vinic acid. When the solution is concentrated it deposites vinate of tin in colourless, flat 6 or 8 sided prisms, easily soluble in water.\*
- 18. Malate of tin. This salt does not crystallize, is very soluble in water, and absorbs moisture from the atmosphere.+
- 19. Succinate of tin. Succinic acid dissolves the oxide of tin when assisted by heat. The solution by evaporation yields thin, broad, transparent crystals. † This salt contained little tin; so that the principal portion remained in solution.
- 20. Benzoate of tin. Neither tin nor its oxide is soluble in benzoic acid; but when benzoate of potash is poured into a solution of tin in nitro-muriatic acid, benzoate of tin precipitates. It is soluble in water by the assistance of heat, but insoluble in alcohol, and decomposed by the action of heat. § Benzoate of potash, when dropt into protochloride of tin, occasions a white precipitate somewhat soluble in hot water, but not in alcohol.
- 21. Camphorate of tin. A white precipitate obtained by double affinity.
- 22. Suberate of tin. Suberic acid throws down protochloride of tin white.
- 23. Pinate of tin, obtained by double affinity, is composed of

Pinic acid . . 100
Protoxide of tin . . 12·1

### SECTION XXVI. -- SALTS OF PEROXIDE OF TIN.

These salts, in their general characters, resemble those of the preceding section. But they are united by a weaker affinity, and few or none of them can be exhibited in a crystallized state. Indeed, so weak is the affinity of peroxide of tin for acids, that it has been frequently considered rather as possessing acid than alkaline characters. The peroxided salts of tin possess the following characters:

- 1. Potash throws down a white precipitate, soluble in an characters. excess of the alkali. But no black powder appears on boiling.
- 2. Ammonia throws down a white precipitate, which is soluble in a great excess of ammonia.

<sup>\*</sup> Waichner. + Braconnot. + Wenzel's Verwandtschaft, p. 241.

<sup>§</sup> Trommsdorf, Ann. de Chim. xi. 315. || Brandes.

<sup>11. 2</sup> 

Class I.

- 3. Prussiate of potash occasions no immediate precipitate; but after some time the whole congeals to a stiff yellow jelly, which is insoluble in muriatic acid.
- 4. Hydrosulphuret of ammonia throws down a yellow precipitate, redissolved by adding an excess of the precipitant. Sulphuretted hydrogen produces no immediate effect, but after some time a yellow precipitate falls.
  - 5. A bar of zinc throws down a white gelatinous precipitate.
- 1. Sulphated peroxide of tin. This salt may be obtained by dissolving hydrated peroxide of tin in dilute sulphuric acid. When the solution is concentrated it is converted into a gelatinous mass. When it is again diluted with water a portion of peroxide of tin separates.
- 2. Nitrated peroxide of tin. Nitric acid dissolves hydrated peroxide of tin, and is completely neutralized. The solution has an astringent taste. When mixed with stronger acid a portion of the nitrated peroxide is thrown down in silky plates. When the solution is heated to 122° almost the whole peroxide falls in the state of a hydrate. If the liquid contains ammonia, this decomposition by heat does not take place.\*
- 3. Selenited peroxide of tin. This salt is a white powder insoluble in water, but soluble in muriatic acid, from which it is precipitated by water. Heat decomposes it.
- 4. Antimoniated peroxide of tin. This compound is obtained when solutions of antimonic acid, and peroxide of tin in muriatic acid are mixed together, and then diluted with water. The two oxides precipitate in combination, leaving the muriatic acid almost in a state of liberty.‡
- 5. Chromated peroxide of tin. Perchloride of tin gives with chromate of potash an orange-yellow precipitate.
- 6. Molybdated peroxide of tin. A gray matter not soluble in water, but soluble in dilute muriatic acid with a blue colour; in concentrated muriatic acid with a green colour; and in potash with a brown colour. Not altered by nitric acid.§
- 7. Iodated peroxide of tin. Iodate of potash throws down a white precipitate when dropt into perchloride of tin.
- 8. Acetated peroxide of tin. A yellow coloured gum like mass.¶
- \* Berzelius. He remarked that the hydrated peroxide thrown down from nitrate by heat is not again soluble in acids till it be treated with ammonia.
  - + Berzelius, Ann. de Chim. et de Phys. ix. 341.

‡ Thenard.

& Berzelius.

Il Pleiscal.

¶ Wenzel.

9. Succinated peroxide of tin. Obtained by double affinity. Sect. XXVII.

A white insoluble powder.

Pinated peroxide of tin. Obtained by double affinity in yellowish-gray flocks. Insoluble in water, oil of turpentine, and fat oils, but soluble (while at the same time it is decomposed) in alcohol and ether.\*

# SECTION XXVII. -- SALTS OF BLACK OXIDE OF COPPER.

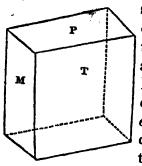
These salts, in consequence of the facility with which copper absorbs oxygen, are in general more easily formed, and of course may be more readily examined than several of the other genera. Hence no doubt the reason that some of them have been so long and so generally employed. The alchymists and the earlier chemists distinguished them by the name of salts of Venus, because Venus was the term which they gave to copper.

The cupreous salts may be distinguished by the following properties:

- 1. They are almost all soluble in water, or at least become Characters. so by the addition of an acid. This solution has either a blue or a green colour, or it acquires that colour after being for some time exposed to the air.
- 2. When ammonia is poured into this solution, it assumes a deep-blue colour.
- 3. Prussiate of potash occasions a red coloured precipitate when poured into a cupreous solution.
  - 4. Hydrosulphuret of potash occasions a black precipitate.
  - 5. Gallic acid occasions a brown precipitate.
- 6. A plate of iron, when plunged into a liquid salt of copper, precipitates the copper in a metallic state.
- 1. Sulphate of copper. Sulphuric acid does not attack copper while cold; but at a boiling heat part of the acid is decomposed, the copper is oxidized, and combines with the remainder of the acid. But recourse is seldom had to this process, as the sulphate of copper is found native abundantly, dissolved in mineral waters connected with copper mines. From these waters it is often obtained by evaporation; or it is formed by burning native sulphuret of copper, or by moistening that sub-

<sup>\*</sup> Unverdorben.

Class I.



stance and exposing it to the air. By either of these methods the sulphur is acidified, and the sulphate of copper formed. This salt appears to have been known to the ancients. In commerce it is distinguished by the name of blue vitriol, and sometimes by that of blue copperas. It has a deep blue colour. It crystallizes readily, and the primary form of the crystal is a doubly oblique prism, as re-

presented in the margin. The following are the measurements of its angles:

P on M	•	•	127°	30'
P on T	•	•	108	00
M on T	•		123	00

The lateral edges of the prisms are often replaced by tangent planes. These crystals reflect doubly.\*

It has a strong styptic metallic taste, and indeed is employed as a caustic. Its specific gravity is 2.23.† 100 parts of water at the temperature of 60° dissolve 45.352 parts of this salt. When exposed to the air, it undergoes a very slight efflorescence, and its surface is covered with a greenish-white powder. When heated, it loses its water, and is converted into a bluish-white powder: if the heat be increased, the acid is driven off, and the black oxide of copper remains behind. The constituents of this salt are as follows:

•	5.625
•	
	•

2. Green sulphate of copper. This salt may be obtained by crystallizing a solution of the preceding in a warm place. It has a green colour. Its crystals are right rectangular prisms, the bases of which are apparently squares. These prisms are small and firm, and are not altered by exposure to the air. When heated, the salt gives out water with a trace of acid, and becomes nearly white. It does not melt. Its constituents are

<sup>\*</sup> Prieur, Ann. de Chim. lxvi. 188.

<sup>†</sup> According to Dr. Watson (Chemical Essays, v. 69).

	1 atom sulphuric acid	•	•	5 5*	Sect. XXVII.
	l atom oxide of copper	•	•	5	
,	l atom water	•	•	1.125	
				11.125	

3. Disulphate of copper. When the crystals of blue sulphate of copper are dissolved in water, and the solution boiled for a long time with a quantity of black oxide of copper, equal to that contained in the salt, the solution becomes at last colourless, and a green coloured powder is deposited, containing all the oxide of copper and all the sulphuric acid. It is therefore a disulphate composed of

4. Tris-sulphate of copper. When a solution of blue sulphate of copper is boiled with oxide of zinc, the latter oxide is dissolved, and a bluish-green precipitate is deposited. When this precipitate is boiled in water as long as the liquid dissolves any thing, it becomes a pure tris-sulphate of copper. Berthollet first pointed out this method of obtaining a subsulphate of copper,\* and Brunner subjected it to analysis, and found its constituents to be

Sulphuric acid	•	•	22.62
Oxide of copper	•	•	65.61
Water	•	•	11.77
			100.00+
This is obviously equivalent to			•
1 atom sulphuric acid		•	5
3 atoms oxide of copper	•	•	15
2 atoms water	•	•	<b>2·25</b> .
			22.25†

This salt may be obtained also by pouring a small quantity of caustic potash into a solution of blue sulphate of copper. was obtained in this way by Proust, and Berzelius showed by an analysis that it is a tris-sulphate of copper containing three atoms of water.

<sup>\*</sup> Ann. de Chim. xlix. 1. † Poggendorf's Annalen, xv. 480.

<sup>‡</sup> The water amounts to 21d atoms; but the excess is doubtless hygrometrical.

5. Tetarto-sulphate of copper. When solutions of sulphate of potash and blue sulphate of copper, in atomic proportions, are mixed together and boiled, the liquid becomes muddy, and a light green powder precipitates, which collects together at the bottom of the vessel. When this precipitate is washed with cold water, and then dried between folds of blotting paper, it still retains some potash, but if it be boiled in repeated portions of water till that liquid ceases to be rendered muddy by chloride of barium or prussiate of potash, it constitutes a simple tetrasulphate of copper, united to a certain quantity of water. This salt was first obtained and analyzed by M. Brunner.

He found its constituents to be

			100.00*
Water	•	•	13.39
Oxide of copper	•	•	67.96
			67.06
Sulphuric acid	•	•	18.65

This is equivalent to

atom sulphuric acid, 1 3.644 atoms oxide of copper, 3.16 atoms water.

Hence I am disposed to consider the true constituents of this salt to be

1 atom sulphuric acid	•	•	5
4 atoms oxide of copper	•	•	20
3 atoms water	•	•	3.375
			28.375

6. Hyposulphate of copper. May be obtained by decomposing hyposulphate of barytes, by means of blue sulphate of copper. By concentrating the solution it may be obtained in doubly oblique prisms, differing very little in their shape from the crystal of blue vitriol. These crystals effloresce somewhat when exposed to the air. The salt is very soluble in water, but insoluble in alcohol. Its constituents, according to the analysis of Heeren, are as follows:

1 atom hyposulphuric acid	•	•	9
1 atom oxide of copper	•		5
4 atoms water	•	•	4.5
·			-
			18.54

<sup>\*</sup> Poggendorf's Annalen, xv. 479.

<sup>†</sup> Ibid. vii. 187.

7. Tetartohyposulphate of copper. When an aqueous solu-sect. xxvii. tion of the preceding salt is mixed with a little ammonia a verdigris-green precipitate falls, which gives a green colour to syrup of violets. It absorbs some carbonic acid gas from the air. When heated it becomes yellow. Its constituents, as determined by the analysis of Heeren, are as follows:

1 atom hyposulphuric acid . 9
4 atoms oxide of copper . 20
4 atoms water . 4.5

33.5\*

8. Nitrate of copper. Nitric acid attacks copper with considerable violence, nitrous gas is emitted in great purity, while the metal is oxidized and dissolved. The solution is of a fine blue colour, and when slowly evaporated yields regular crystals of nitrate of copper.

These crystals are flat four-sided prisms, apparently rectangular. Their specific gravity is 2.174.+ They have a fine blue colour, their taste is acrid and metallic, and they are exceedingly caustic, corroding the skin with great energy. They are very soluble in water, and when exposed to the air gradually attract moisture and deliquesce. At a heat not exceeding 100° they undergo the watery fusion, and if the heat be increased they lose their water and part of their acid. On burning coals they detonate feebly. These crystals detonate also when mixed with phosphorus and struck with a hammer, as Brugnatelli first observed. When a quantity of them, moistened with water, is wrapped up in a sheet of tinfoil, they act with amazing energy upon that metal, nitrous gas is emitted, a strong heat is produced, the tinfoil is burst open in every direction, and very often it takes fire. This curious experiment was first made by Dr. Higgins.‡

The constituents of this salt, according to my analysis, are

1 atom nitric acid . . . 6.75
1 atom oxide of copper . . . 5
7 atoms water . . . 7.875

19.625

9. Trisnitrate of copper. This salt is obtained when we cautiously heat the preceding salt till it ceases to be soluble in water. It is a soft blue-coloured powder, composed of

<sup>\*</sup> Poggendorf's Annalen, vii. 187.

<sup>†</sup> Hassenfratz, Ann. de Chim. xlii. 218. ‡ Phil. Trans. lxiii. 137.

. Class I.

l_atom nitric acid		•	6.75
satoms oxide of copper	•	•	15
4 atoms water	•	•	4.5
			96.9%

10. Tetartonitrate of copper. This salt may be obtained by precipitating nitrate of copper by ammonia, washing the precipitate with water, and drying it in a gentle heat. It is a beautiful light copper-green insoluble powder. Its constituents are

1	atom nitric acid	•	•	6.75
4	atoms oxide of copper	•	•	20
5	atoms water	•	•	5.625
				99.975

11. Pentanitrate of copper. When potash is poured into a solution of nitrate of copper a blue precipitate appears, which soon becomes green by agitation, provided the quantity of potash be insufficient to decompose the whole of the nitrate. Mr. Proust has proved that this green precipitate is a subnitrate of copper. It may be obtained also by distilling nitrate of copper in a retort. At a particular period of this process the salt becomes thick, and encrusts the retort in the state of a green lamellar concretion. It is then converted into subnitrate. This salt is completely insoluble in water. Sulphuric acid separates its acid, and the same separation may be effected also by distillation. Berzelius likewise examined this subnitrate, which he obtained by various processes, but found it always the same. Its constituents are as follows:

1 atom nitric acid	•	•	<b>6·75</b>
5 atoms oxide of copper		•	<b>25</b>
5 atoms water	•	•	5.625
			05 05 1

- 12. Hyponitrite of copper. When hyponitrite of lead and blue vitriol are mixed in the atomic proportions we obtain a green-coloured solution, which when heated, is converted into nitrate of copper.†
- 13. Chlorate of copper. Peroxide of copper dissolves readily in chloric acid. It is not possible to neutralize the acid by this oxide. The salt does not crystallize readily. Its colour is green. On burning coals it fuses slightly, and gives out a

<sup>\*</sup> Berzelius, Ann. de Chim. lxxxii. 250. † Berzelius,

green light. Paper dipped into the solution of this salt burns sect. XXVII. with a fine green flame, at a temperature inferior to what would be requisite to set fire to the paper itself.\*

14. Iodate of copper. When solutions of sulphate of copper and iodate of potash are mixed a precipitate falls, which is

soluble in acids.+

15. Hydrous-dicarbonate of copper. Carbonic acid does not attack copper, but it combines readily with its oxide, or with the hydrate of copper, when that compound is mixed with water, and a current of carbonic acid gas made to pass through Or the carbonate may be formed by precipitating a solution of nitrate of copper with a fixed alkaline carbonate. give the carbonate all its lustre, the solution should be mixed with boiling water, and the precipitate should be washed with great care, and exposed to the light of the sun. It has then a fine apple-green colour, and it is found often native in its greatest beauty. The native hydrous carbonate is known among mineralogists by the name of malachite. It is insoluble in water, and is converted to black oxide of copper by the action of heat. It occurs occasionally crystallized, and the primary form of the crystal is an oblique rhombic prism, the base of which is inclined to the lateral faces at angles of 112° 52'. and the inclination of the faces of the prism is 107° 20'. Its specific gravity is about 4, and it has an emerald-green colour. The constituents of this salt are

1	atom carbonic acid	•	•	2.75
<b>2</b>	atoms oxide of copper	•	•	<b>10</b> ·
1	atom water	•	•	1.125
				-
				13.875

16. Anhydrous-dicarbonate of copper. When the preceding salt in fine powder is boiled for some time in water, it becomes brown. MM. Colin and Taillepert have shown that when thus treated, it is anhydrous, and composed of

1 atom carbonic acid	•	•	•	2.75
2 atoms oxide of copper	•	•	•	10
				12·75§

<sup>\*</sup> Vauquelin, Ann. de Chim. xcv. 133. + Gay-Lussac, ibid. xci. 86.

<sup>‡</sup> Mr. Chenevix has shown that the alkaline carbonates have the property of dissolving a portion of the oxide of copper, and of forming with it a triple salt.

<sup>§</sup> Ann. de Chim. et de Phys. xii. 62.

Class I.

This anhydrous dicarbonate exists in India in considerable quantity. It is in brown amorphous masses, mixed generally with a little peroxide of iron, running through it in small veins. Often also thin veins of malachite traverse it irregularly.

17. Hydrous-subsesquicarbonate of copper. This salt is prepared artificially, and sold under the name of blue verditer, but the process is kept secret. It is prepared by silver refiners from the solution of nitrate of silver remaining after precipitating the silver from nitric acid. It exists native in some quantity, and is known by the name of blue copper ore. It is a fine azure-blue mineral, sometimes opaque, but often translucent, and crystallized in oblique rhombic prisms approaching the cube. The base of the prism makes with the lateral faces an angle of 91° 30′, and the two contiguous lateral faces meet at angles of 99° and 81°. It is harder than calcareous spar, and has a specific gravity of 3.831. Its constituents, according to the analysis of Mr. Phillips, are

1	atom	carbonic acid	•	•	2.75
$1\frac{1}{2}$	$\mathbf{atom}$	oxide of copper	•	•	7.25
1/2	atom	water	•	•	0.5625

10.5625\*

18. Hydrated diphosphate of copper. This salt was discovered in 1812 in the mine of Liebethen in Hungary by M. Rosner. It is crystallized in octahedrons with a rectangular base, the faces of which (at the base) are inclined to each other at angles of 100° to 110°. Its colour is greenish-black, and it has considerable lustre. When calcined it assumes a beautiful grass-green colour. Its constituents, as determined by Berthier, are

Phosphoric acid	•		28.7
Oxide of copper	•	•	63.9
$\mathbf{Water}$	•	•	7.4
			100.0+
This is obviously equivalent to			
1 atom phosphoric acid	•	•	4.5
2 atoms oxide of copper	•	•	-10
l atom water	•	•	1.125
			***************************************

<sup>\*</sup> Institution Journal, iv. 273.

15.625

19. Hydrous trisphosphate of copper. This salt occurs native sect. XXVII. in veins, traversing gray-wacke slate near Rheinbreitbach on the Rhine. The colour is green of various shades, and the streak green, but a little pale. It occurs crystallized, and the primary form of the crystal is an oblique rhombic prism. The base is inclined to the lateral faces of the prism at an angle of 97° 30′, and the two contiguous faces of the prism meet at angles of 37° 30′ and 142° 30′, according to the measurements of Mr. Brooke. Its specific gravity is 4·205, as determined by Mr. Haidinger. We have three analyses of this mineral, but they differ so much, that it is impossible to deduce from them the true composition. These analyses are as follows:

Phosphoric acid . 30.95 . 21.687 . 24.7 Oxide of copper . 68.13 . 62.847 . 68.2 Water . 0.00 . 15.554 . 5.97

99.08\* 100.088† 98.87‡

If we take Mr. Lunn's analysis as representing the true constitution of the mineral, we have the constituents as follows:

1 atom phosphoric acid . 4.5
3 atoms oxide of copper . 15
3 atoms water . . 3.375

22.875

100.08

20. Subsequiphosphate of copper. This salt may be obtained with great facility by pouring phosphate of soda into a solution of nitrate of copper. A bluish-green powder immediately precipitates, and the liquid becomes acid. This salt is insoluble in water. When exposed to a red heat, it loses its water, and acquires a brown colour. When violently heated, phosphuretted copper comes over. According to the analysis of Mr. Chenevix, it is composed of

This is equivalent to

atom phosphoric acid,1·14 atom oxide of copper,1·772 atom water.

<sup>\*</sup> Klaproth, Beitrage, iii. 201. † Lunn, Edin. Phil. Jour. v. 213. † Arfvedson. † Phil. Trans. 1801, p. 206.

But from the experiments of Mitcherlich there is reason to consider it as a subsesquiphosphate, or a compound of

1 atom phosphoric acid	•	4.5
$1\frac{1}{a}$ atom oxide of copper	•	<b>7·5</b>
3? atoms water .	•	3.375
		15.375

- 21. Biphosphate of copper. The solution of the preceding salt in phosphoric acid when evaporated leaves a green gummy
- 22. Arseniated copper. No fewer than 5 different species of arseniated copper occur in the mineral kingdom. I shall merely give the name and constituents of each here. description will be given when treating of mineralogy.
  - (1.) Quaterhydrated diarseniate, composed of

1 atom arseni	acid		•	7.25
2 atoms oxide	of copper	r	•	10
4 atoms water	•	•	•	4.5
				21.75

(2.) Terhydrated diarseniate of copper, or copper mica, composed of

	1 atom arsenic acid	7.25
	2 atoms oxide of copper .	10
	3 atoms water	3.375
		$\overline{20.625}$
)	Prismatic oliven ore, composed of	= 0=

(3.)

2 atoms oxide of		• r .	•	7.25 10
$1\frac{1}{2}$ atom water	•	•	•	1.6825
				18.9325

(4.) Acicular oliven ore. composed of

cecular occore ore, composed	O1	
1 atom arsenic acid .	•	7.25
2 atoms oxide of copper	•	10
2 atoms water	•	2.25
•		

19.5

(5.) Octahedral arseniate, or linzenerz, composed of

When nitrate of copper and arseniate of ammonia are mixed together, a precipitate falls. When the liquid portion is separated from this precipitate, and after concentration mixed with alcohol, blue rhomboidal crystals are obtained of arseniated copper. But not having been subjected to analysis, we do not know whether they are similar to any of the five preceding species.

- 23. Arsenite of copper. Arsenious acid forms with oxide of copper an arsenite, usually distinguished by the name of Scheele's green, because Mr. Scheele first examined it, and proposed it as a paint. It may be formed by dissolving two parts of sulphate of copper in 44 parts of water, and likewise two parts of potash of commerce and nearly one part of the white oxide of arsenic pulverized, in 44 parts of water by the assistance of heat. The solution of copper is gradually added while hot to the arsenite of potash, and the whole is often stirred during the mixture. The mixture, on standing, gradually deposites the arsenite of copper in the form of a fine green powder. It is to be washed well with water and then dried.\*
- 24. Superarsenite of copper. A solution of carbonate of copper, in an excess of arsenious acid and water, is neither precipitated by acids nor alkalies, and when concentrated, deposites a yellowish-green salt.+
- 25. Borate of copper. When borax is poured into a solution of sulphate of copper, borate of copper is precipitated in the form of a pale light-green jelly, which when dried is with great difficulty soluble in water. It easily melts into a dark-red vitreous substance.‡ According to Palm, by long trituration of filings of copper and boracic acid in water, and then digesting the mixture, it dissolves, and crystals may be obtained from it.
- 26. Silicated copper. Two species of silicated copper occur in the mineral kingdom; namely,
  - (1.) Hydrous sesquisilicata, or dioptase, composed of

<sup>\*</sup> Scheele, i. 261.

<sup>+</sup> Berzelius.

Class I.	11	atom	silica	•	•	•	<b>3</b> .
	1	atom	oxide	of copper	J.	•	<b>5</b>
r	1	atom	water	•	•	•	1.125
							9.125

(2.) Hydrous bisilicate of copper, or kieselmalachite, composed of

27. Selenite of copper. When a hot solution of sulphate of copper is mixed with biselenite of ammonia, a yellow precipitate falls in very bulky flocks. This precipitate rapidly diminishes in volume, and is converted into very brilliant small silky crystals of a greenish-blue colour. These crystals consist of neutral selenite. This salt is neither soluble in water, nor in selenious acid. When heated, the water of crystallization escapes, and the salt becomes liver-brown. At a higher temperature, it melts and becomes black. It then begins to boil, gradually allows its acid to escape, and at last nothing remains but peroxide of copper.

28. Disclenite of copper. It is obtained by precipitating sulphate of copper by disclenite of ammonia. It is an insoluble pistachio-green powder, but soluble in ammonia. When heated, it becomes black, and allows its water to escape: then it swells up, and its acid is disengaged.\*

29. Antimoniate of copper. Antimoniate of potash, when dropped into sulphate of copper, occasions a precipitate of antimoniate of copper. It is a bulky green precipitate, quite insoluble in water. When heated, it loses 19 per cent. of water. Before the blow-pipe on charcoal it is reduced with a lively deflagration, leaving a metallic button composed of copper alloyed with antimony.†

30. Antimonite of copper. This salt may be prepared in the same way as the preceding species, which it resembles in its colour and insolubility in water. A subantimonite of potash precipitates a subantimonite of copper, which resembles arsenite of copper in its appearance.

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. p. 340.

<sup>+</sup> Ibid. Nicholson's Jour. xxxv. 43.

- 31. Tellurate of copper. Tellurate of potash occasions a Sect. XXVII. beautiful emerald-green precipitate when dropped into sulphate of copper. This precipitate is tellurate of copper. When heated, it gives out water, and becomes black. When more strongly heated, it melts into a black glass. When heated on red-hot charcoal, it is reduced with detonation like nitre, and leaves an alloy of tellurium and copper of a pale red colour.\*
- 32. Chromate of copper. This salt may be obtained by mixing solutions of chromate of potash and chloride of copper. The precipitate which falls has a fine buff colour, with a shade of red. It has a slightly sweetish taste, and is somewhat soluble in water. It does not affect vegetable blues. Its constituents, by my analysis, are

1	atom chromic acid		•	<b>6·5</b>
1	atom oxide of copper	_ (	•	5
2	atoms water .			2.25
				13.75

- 33. Molybdate of copper. A yellowish-green precipitate, difficultly soluble in water, and decomposed by acids and bases.+
- 34. Tungstate of copper. Tungstic acid and its compounds occasion a white precipitate when poured into the salts of copper.‡
- 35. Oxalate of copper. Oxalic acid is capable of attacking copper, and forming with it needle-shaped crystals of a green colour, not altered by exposure to the air.§ It combines with great facility with its oxide. The oxalate formed is in the state of a bluish-green powder, scarcely soluble in water unless with excess of acid. Oxalic acid precipitates this salt from liquid sulphate, nitrate, muriate, and acetate of copper.

When this salt is obtained by mixing together solutions of oxalate of ammonia and sulphate of copper, it is a green, tasteless, insoluble powder, composed of

1 atom oxalic ac	eid	•	. •	4.5
1 atom oxide of	copper		•	5
1 atom water	•	•	•	1.125
				10:625
				コルカツカ

One half of the water is easily expelled by heat; but the re-

1 Scheele.

<sup>\*</sup> Berzelius, Nicholson's Journal, xxxvi. 131.

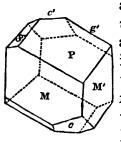
<sup>+</sup> Berzelius.

<sup>§</sup> Wenzel, Ann. de Chim. xi. p. 229.

Class I. mainder continues obstinately fixed till the acid undergoes

decomposition.

36. Acetate of copper. Acetic acid attacks copper very slowly in open vessels, converts it into an oxide, and dissolves it: but in close vessels no action takes place. This acid readily combines with the oxide of copper, and forms with it an acetate. This salt was known to the ancients, and various ways of preparing it are described by Pliny.\* It is usually obtained by exposing plates of copper to the action of vinegar till they



are converted to a bluish green powder called verdigris, and then dissolving this powder in acetic acid, and crystallizing it. It crystallizes in oblique rhombic prisms, as represented in the margin, where it is slightly modified by a few secondary faces. The measurements of the angles of this crystal, as made by Mr. Brooke, † are as follows:

P on M or M'	•	•	105°	30
M on M'	•	•	<b>72</b>	0
P on c	•	•	119	4
P on g or g'	•	•	131	<b>45</b>

It has a beautiful bluish-green colour. Its specific gravity is 1.914.‡ Its taste is disagreeably metallic, and, like all the compounds into which copper enters, it is poisonous. It is sparingly soluble in cold water. When that liquid is boiled upon the salt, it takes up, according to Wenzel, ½th of its weight of it.§ Alcohol likewise dissolves it. When exposed to the air, it effloresces. By distillation it gives out acetic acid. Proust first remarked that acetous acid and acetic acid form the same salt with copper; and hence concluded that there is no difference between the two acids. When sulphuretted hydrogen gas is made to pass through a solution of this salt in water, the copper is deoxidized, and precipitates in the state of a black sulphuret, and there remains behind an acid which possesses the properties of the acetic. ¶

From the analysis of this salt by Phillips \*\* and Berzelius, †† it is evident that its constituents are

<sup>\*</sup> Lib. xxxiv. c. 11. † Annals of Philosophy (2d series), vi. 39.

<sup>‡</sup> Gehlen. § Verwandtschaft, p. 310.

Jour. de Phys. lvi. 211. ¶Ann. de Chim. xxxii. 36.

<sup>\*\*</sup> Annals of Philosophy (2d series), i. 417. †† Ibid. viii. 192.

1 atom acetic acid . 6.251 atom oxide of copper 5 l atom water 1.125 12:375 Sect. XXVII.

37. Diacetate of copper. This is the pigment called verdigris, which is prepared in the large way as a paint. It may be formed by placing layers of acetate of copper and copper plates, moistened with water, and leaving them in a damp place. It is a soft silky matter, of a fine blue colour, composed of small needle-form crystals. With a little water it swells up, and if more be added a portion is dissolved, and a green or blue powder remains undissolved. Its constituents, as determined by the analysis of Phillips,\* with which that of Berzelius+ corresponds, are as follows:

			23.
		•	
6 atoms water	•	•	6.75
2 atoms oxide of copper	•	•	10
1 atom acetic acid	•	•	6.25

Green verdigris is not a chemical compound, but a mechanical mixture.

38. Subsesqui-acetate of copper. When the preceding salt is digested in water, it is decomposed into two new salts, one of which is insoluble, while the other dissolves in the water. When the aqueous solution is concentrated till the greater part of its saline contents is deposited, by applying heat the whole is dissolved. When alcohol is mixed with this solution, and the mixture set aside, in about an hour a gelatinous looking mass is deposited, consisting of an aggregation of minute crystals. When dry they have a pale blue colour. Berzelius subjected them to analysis, and found their constituents as follows:

l atom acetic acid	•	•	6.25
$l^{\frac{1}{2}}$ atom oxide of copper	•		7.50
3 atoms water	•	•	<b>3·375</b>

17·125±

39. Trisacetate of copper. This is the insoluble salt obtained when verdigris is treated with water. If we pour the whole on coarse linen, the insoluble salt passes along with the water,

<sup>\*</sup> Annals of Philosophy (2d series), iv. 161. + Ibid. viii. 198. ‡ Ibid. p. 194. 2 xII.

while the impurities are left behind. A second filtration through fine cambric retains the insoluble salt. It must be washed first in water, and then transferred to a paper filter, and thoroughly washed with alcohol. The salt thus obtained constitutes a mass of light blue shining crystalline scales, having a deeper and purer blue than the subsesquiacetate. When dried in 212° it loses a little hygroscopic water, and does not alter its appearance. Its constituents, as determined by the analysis of Berzelius, are

1 atom acetic acid	•	•	6.25
3 atoms oxide of copper	•		15
2 atoms water	•	•	2.25
			<del></del>
			23.5*

- 40. Lactate of copper. When lactic acid is digested on copper, it assumes first a blue colour, and then a green, which passes into a dark brown; but the solution does not crystallize.+
- 41. Formate of copper. This salt has a greenish-blue colour, is transparent, and crystallizes in rectangular tables with bevelled edges, constituting an octahedron with a rectangular base, the two summits of which are deeply truncated. The specific gravity of the crystals is 1.815. When exposed to the air they effloresce. When heated they burn with a green coloured flame.‡ They are soluble in 8.4 times their weight of cold water, according to the determination of Gehlen, and in about 400 times their weight of weak alcohol. The constituents of this salt, as determined by the analysis of Göbel, with which the previous experiments of Gehlen nearly coincide, are as follows:

1 atom formic acid	•	•	4.625
1 atom oxide of copper	•	•	5
4 atoms water	•	•	4.5
			14.105

- 42. Subformate of copper. A greenish powder, not easily soluble in water.
- 43. Mellate of copper. When mellate of ammonia and sulphate of copper are mixed together, a bulky, very light blue precipitate falls, which, when well washed on the filter, contracts in its dimensions, and is converted into a light blue crys-

<sup>\*</sup> Annals of Philosophy (2d series) iv. p. 198.

talline powder. It contains 20 per cent. of water of crystalli- Sect. XXVII. zation. It dissolves readily in ammonia, and when the solution is concentrated, rhombic crystals of ammonio-formate of copper are deposited.\*

44. Tartrate of copper. When dilute solutions of sulphate of copper and tartrate of potash are mixed, small green crystals of tartrate of copper are gradually deposited. They are very little soluble in water. They are composed of

1 atom tartaric acid	•	•	$8 \cdot 25$
1 atom oxide of copper	•	•	5
3 atoms water	•	•	3.375
			16:625

- 45. Bitartrate of copper. When to the solution of the preceding salt tartaric acid is added, the bitartrate is deposited in the state of a bluish-white powder.† This salt is soluble in nitric acid; but not in water nor tartaric acid.
- 46. Vinate of copper. Vinate of potash throws down a precipitate when dropt into sulphate of copper.;
- 47. Pyrotartrate of copper. Pyrotartrate of potash throws down a fine green precipitate when poured into nitrate of copper. The constituents of this salt, according to the analysis of Göbel, are

Pyrotartaric acid	•	•	$62 \cdot 24$
Oxide of copper	•	•	37.76
			100.00

- 48. Citrate of copper. Light green crystals.§
- 49. Malate of copper. A green matter, not capable of crystallizing, and not altered by exposure to the air.
  - 50. Bimalate of copper. It does not crystallize.
- 51. Fungate of copper. Sulphate of copper is not precipitated by fungic acid.
- 52. Mucate of copper. Sulphate of copper is not precipitated by mucic acid, but it is thrown down by mucate of potash.
- 53. Dimucate of copper. When carbonate of copper, mucic acid, and water are boiled together, an apple-green powder is formed, not soluble in water. It is composed, according to the analysis of Tromsdorf, of
  - \* Wöhler. † Thenard. ‡ Walchner. \$ Wenzel's Verwandtschaft, p. 185. | Braconnot. ¶ Ibid.

Class 1.

54. Pyromucate of copper. Small greenish-blue crystals, little soluble in water.\*

- 55. Succinate of copper. Succinic acid dissolves copper with difficulty, and only when assisted by a long digestion. The solution is green, and yielded Wenzel small green crystals, the properties of which have not been examined. From the experiments of the same chemist we learn, that there are two varieties of this salt, a supersuccinate and a subsuccinate. He digested 10 grains of carbonate of copper in succinic acid: an effervescence took place; one portion was dissolved, but another remained at the bottom of the vessel. This portion weighed 17 grains. It had lost its carbonic acid, and evidently contained succinic acid. The solutions contained a portion of copper, which was not separated by an alkali, but by a hydrosulphuret, and zinc threw it down.†
- 56. Benzoate of copper. Benzoic acid does not act upon copper, but it combines readily with the oxide of that metal. The salt formed is in small crystals of a deep-green colour, sparingly soluble in water, and insoluble in alcohol. When heated the acid evaporates and leaves the oxide. The alkalies and the carbonates of lime and barytes decompose it. When benzoate of potash and sulphate of copper are mixed, this salt precipitates in the state of a bluish powder, which becomes a fine green on drying, and, according to Berzelius, is somewhat soluble in water.
- 57. Gallate of copper. Sublimed gallic acid when added to acetate of copper, throws down beautiful brown flocks.
- 58. Meconate of copper. When meconic acid is added to sulphate of copper, the liquid assumes a beautiful emerald-green colour, and after some time a yellow precipitate falls.
- 59. Boletate of copper. When boletate of potash is added to a solution of nitrate of copper, blue silky needles fall, very little soluble in water.
  - 60. Camphorate of copper. When solutions of camphorate

<sup>\*</sup> Labillardiere.

<sup>†</sup> Wenzel's Lehre von der Verwandtschaft der Korper. Grindel's edit. p. 242.

<sup>‡</sup> Trommsdorf, Ann. de Chim. xi. 315.

<sup>§</sup> Robiquet.

of potash and sulphate of copper are mixed, a light green precipitate falls. When heated it becomes azure-blue, and by a
stronger heat, dark-green, then white, and at last black, when
it catches fire and burns with a pale flame and much smoke.
The salt is insoluble in water. Its constituents are

Camphoric acid . . . 70·418 Oxide of copper . . . 29·582

100.000\*

61. Suberate of copper. Suberate of ammonia throws down a light blue precipitate from the cupreous salts. When dry it is bluish-green, and is composed of

It is little soluble in water. When heated it melts and undergoes decomposition.+

62. Butyrate of copper. It may be obtained by dissolving carbonate of copper in an aqueous solution of butyric acid. It crystallizes in eight-sided prisms, with an oblique base. When kept in vacuo over sulphuric acid it loses 1 per cent. of its weight; and becomes less transparent. When heated to 212° it loses no acid. But at that temperature the aqueous solution becomes muddy and deposites oxide of copper. It is composed, according to Chevreul, of

Butyric acid		•	<b>57·04</b>
Oxide of copper	•	•	29.63
Water	•	•	13.33
7331 • • • • • • • • • • • • • • • • • •			100.00‡
This is equivalent to			
1 atom butyric acid	•	•	9.625
1 atom oxide of copper	٠.	•	10

21.875

63. Cholesterate of copper. An olive-green salt.

64. Pinate of copper. An alcoholic solution of pinic acid when boiled over oxide of copper gradually combines with it.

2 atoms water

<sup>\*</sup> Brandes, Schweigger's Jour. xxxviii. 297.

<sup>+</sup> Ibid. xxxiii. 97.

<sup>‡</sup> Sur les corps gras, p. 130.

An ethereal solution of pinic acid dissolves carbonate of copper with effervescence. It decomposes also borate and benzoate of copper. We may obtain pinate of copper by mixing pinate of potash with an aqueous solution of a cupreous salt. It is a green powder, which at 212° begins to concrete, and in a higher temperature is converted into a resinous looking mass, of a darker-green colour. In a still higher temperature it is converted into pinated suboxide of copper. It is insoluble in water, very little soluble in absolute alcohol or naphtha, but very soluble in ether, oil of turpentine, and fat oils. The ethereal solution is dark-green, and when concentrated, deposites the salt in crystalline sphericles. When the solution in oil of turpentine is exposed to the air it gradually dries into a green transparent varnish.\* This salt is composed of

Pinic acid . . . 100 Oxide of copper . . . 7.4

65. Silvate of copper. Very similar to the preceding salt. It is soluble in absolute alcohol, from which it is deposited by spontaneous evaporation in brilliant crystalline grains. Its solution in ether has more of a blue colour than that of pinate of copper.+

- 66. Carbazotate of copper. This salt is obtained by mixing solutions of sulphate of copper and carbazotate of barytes in the requisite proportions. The crystals form with difficulty. They have a fine green colour, and deliquesce in the air. When heated the salt undergoes decomposition without burning with flame.‡
- 67. Pyrurate of copper. Pyrurate of potash throws down a precipitate when dropped into sulphate of copper.
- 68. Hydro-carbo-sulphate of copper. Hydro-carbo-sulphate of potash throws down a fine yellow precipitate when dropped into a cupreous salt.
- 69. Sulphovinate of copper. This salt may be formed by dissolving carbonate of copper in sulphovinic acid, and evaporating the solution. It crystallizes in blue coloured four-sided tables with sharp edges. It is very soluble in water, it dissolves also in alcohol. When heated to redness it burns with flame and leaves sulphate of copper.

<sup>\*</sup> Unverdorben, Poggendorf's Annalen, xi. 233. † Ibid. p. 400.

Liebig, Ann. de Chim. et de Phys. xxxv. 84.

<sup>§</sup> Chevallier and Lassaigne, ibid. xiii. 160.

Zeise, Annals of Chemistry (2d series), iv. 242.

<sup>¶</sup> Vogel, Gilbert's Annalen, lxiii. 95.

- 70. Sulphonaphthalate of copper. Hydrated oxide of copper Sect.XXVIII. forms an acid salt when digested in sulphonaphthalic acid, and the solution by spontaneous evaporation leaves radiated crystalline films. The dry salt when heated fuses and burns with flame.\*
- 71. Sinapate of copper. When sinapic acid is added to a solution of sulphate of copper it changes its colour to green, and in about an hour a white powder is deposited.

#### SECTION XXVIII.—SALTS OF SUBOXIDE OF COPPER.

This genus of salts has been very little investigated. These salts, so far as known at present, are never green or blue, but red, brown, or black. When exposed to the air they speedily absorb oxygen, and are converted into the corresponding salts of black oxide of copper.

- 1. Sulphated suboxide of copper. This salt may be obtained by decomposing sulphate of copper by means of phosphorus. A black powder falls, which requires to be rapidly washed and dried. It dissolves in nitric acid with the evolution of deutoxide of azote.‡
- 2. Sulphited suboxide of copper. Sulphurous acid combines only with the suboxide of copper, the black oxide having the property of converting it into sulphuric acid. Sulphited suboxide of copper may be formed by passing a current of sulphurous acid gas through water containing black oxide of copper mixed with it. The oxide is gradually converted into suboxide by giving out one half of its oxygen to a portion of the sulphurous acid, which it converts into sulphuric. The sulphited suboxide of copper remains in the state of small red crystals, while the sulphate dissolves in the water. This salt. may be obtained also by mixing a solution of sulphate of potash with a solution of nitrate of copper, and washing the yellow precipitate that falls till it becomes red. It is in the state of small red crystals. It is insoluble in cold water, but when long boiled in water, the whole of its acid is separated and nothing remains but suboxide of copper. When heated it gives out water, sulphurous acid, a little sulphur, and some sulphate of copper is formed. Potash and soda readily deprive it of its acid. Chlorine and nitric acid convert it into sulphate of copper. According to Chevreul, to whom we are indebted for the whole of the preceding facts, this salt is composed of
  - \* Faraday, Annals of Philosophy (2d series), xii. 210.
  - † Henry and Garot. · ‡ Berzelius, Ann. de Chim. et de Phys. ii. 228.

Class I.	Sulphurous acid	•	•	<b>32·1</b> 8
	Suboxide of copper	•	•	56.82
•	Water .	•	•	11.00
		•		
				30000

100.00\*

15.6825

If we reckon the atomic weight of suboxide of copper 9, this is equivalent to

$1\frac{1}{4}$ atom sulphurous acid	•	<b>5</b> .
1 atom suboxide of copp	per .	9
$l_{2}^{1}$ atom water	•	1.6825

- 3. Hyposulphited suboxide of copper. This salt may be formed by digesting hyposulphite of lime on carbonate of copper, or by mixing sulphate of copper with hyposulphite of lime, potash, &c. It is colourless, of an intensely sweet taste, followed by a mawkish sweetness like liquorice root, but with no metallic flavour. It is not decomposed, nor turned blue by ammonia.
- 4. Nitrated suboxide of copper. This salt does not exist, because nitric acid has the property of converting suboxide of copper into black oxide.
- 5. Selenited suboxide of copper. This salt may be formed by digesting hydrated suboxide of copper in selenious acid. It is a white powder, not soluble in water.
- 6. Acetated suboxide of copper. When crystallized verdigris is distilled this salt sublimes towards the end of the distillation in white flocks, which, according to Berzelius, contain no water. Its taste is caustic and astringent, and it reddens litmus paper. It undergoes no change when exposed to the air. When water is poured on it suboxide of copper precipitates in yellow flocks. It is partially soluble in alcohol, leaving a yellow powder undissolved.†

This salt was mistaken by Proust for anhydrous acetate of copper.

7. Vinated suboxide of copper. Copper dissolves very slowly in vinic acid. After some days the solution deposites a greenish-blue salt, and then by concentration deposites white oblique rhombic prisms, soluble in water, and precipitated by potash in yellow flocks.‡

<sup>\*</sup> Ann. de Chim. Ixxxiii. 181. † Berzelius and Gehlen.

<sup>‡</sup> Walchner.

8. Pinated suboxide of copper. When pinic acid is fused with carbonate or acetate of copper till the acids are expelled, and the mixture, at first green, has become brown and transparent, and the excess of pinic acid is removed by alcohol, pinated suboxide of copper is formed. A brownish-yellow powder. It is but little soluble in ether, but more soluble in oil of turpentine. The solutions speedily absorb oxygen and become green.\*

9. Silvated suboxide of copper. Easily soluble in ether.+

# SECTION XXIX. - SALTS OF OXIDE OF BISMUTH.

The salts of bismuth may be distinguished by the following properties:

- 1. The solution of bismuth in acids is usually colourless. Characters. When water is poured into it a white precipitate immediately falls, consisting chiefly of the white oxide of bismuth.
- 2. Prussiate of potash occasions in these solutions a precipitate of a white colour, sometimes with a shade of yellow.
- 3. Hydrosulphuret of potash and sulphuretted hydrogen occasion a dark-brown precipitate.
- 4. Gallic acid and the infusion of nut-galls occasion an orange-yellow precipitate.
- 5. When a plate of copper or tin is put into the solution of bismuth, this last metal is often precipitated in the metallic state.
- 1. Sulphate of bismuth. This salt may be obtained by heating bismuth in sulphuric acid. The metal is converted into a white powder, while at the same time sulphurous acid is exhaled, and even sulphur sublimed, if the heat be considerable. When the saline mass thus formed is washed with water, two thirds of the acid are separated, carrying along with them a very small portion of the oxide, and this lixivium yields by evaporation small crystals in needles, which are decomposed, and their base precipitated when any attempt is made to dissolve them in water.

According to the experiments of Lagerhjelm, the sulphate of bismuth is composed of

Sulphuric acid . . . . 100
Oxide of bismuth . . . 197.5

This is obviously

\* Unverdorben, Poggendorf's Annalen, xi. 233. † Ibid. p. 400.

1 atom sulphuric acid	•	•	5
l atom oxide of bismuth	•	•	10
			15

2. Trissulphate of bismuth. When the preceding salt is digested in water a white insoluble powder remains, which when heated, gives off sulphurous acid and oxygen gas. It is composed, according to the experiments of Berzelius,\* of

1 atom sulphuric acid		•	5
3 atoms oxide of bismuth	• ,	•	30
			35

- 3. Sulphite of bismuth. Sulphurous acid does not attack bismuth, but it combines with its oxide, and forms with it a salt insoluble in water, even when assisted by an excess of acid. It has a sulphureous taste, and before the blow-pipe melts into a reddish-yellow mass, which is soon reduced upon charcoal. When distilled, the acid is driven off, and the whole oxide remains in a state of purity.+
- 4. Nitrate of bismuth. Nitric acid when concentrated attacks bismuth with great violence, a vast quantity of nitrous gas is emitted, the metal is converted into a white oxide, much heat is evolved, and sometimes even sparks of fire, it is said, are darted out of the mixture. When the acid is diluted, the action is less violent, and the oxide of bismuth is dissolved as it forms. The solution is colourless, and on cooling lets fall crystals of a white colour, and generally attached to cach other in the form of stars. The crystals are pretty oblique rhomboidal prisms, quite transparent and colourless. salt, when exposed to the air, attracts a little moisture, and its surface is covered with a crust of white hydrated oxide. burning coals it detonates feebly, emitting red sparks, and leaves a yellowish powder not easily reduced. turated with phosphorus it detonates loudly. When put into water it is immediately decomposed, that liquid absorbing its acid, and leaving the white hydrated oxide of bismuth combined with a small portion of acid. Hence the reason, that when we write upon paper with a solution of bismuth in nitric acid, the characters, at first invisible, become white when the paper is plunged into water, as Brugnatelli first observed.§
  - \* Ann. de Chim. lxxxii. 241.

<sup>+</sup> Fourcroy, v. 204.

<sup>.†</sup> Brugnatelli, Ann. de Chim. xxviii. 73.

<sup>§</sup> Ibid. iii. 296.

When the solution of bismuth in nitric acid is diluted with sect. XXIX. water, the greatest part of the metal separates in the state of a subnitrate. In this state it was formerly known by the name of magistery of bismuth.

The constituents of this salt are

1 atom nitric acid	•	•	6.75
1 atom oxide of bismuth		•	10
3 atoms water •	•	•	3.375
			00.102

5. Supernitrate of bismuth. When nitrate of bismuth is digested in water it undergoes decomposition, a subnitrate remains undissolved, and a supernitrate is held in solution by the water. This last salt may be obtained by evaporating the liquid, but it has not been examined. From the analytical experiments of M. Grouvelle, it appears that this supernitrate is a compound of

		77.5*
1 atom oxide of bismuth	•	10
10 atoms nitric acid.	•	67.5

6. Dinitrate of bismuth. I obtained this salt in crystals from a rather strong solution of bismuth in nitric acid freeing it from all excess of acid by pressure between folds of blotting paper. Its constituents were found to be

l atom nitric acid	•	•	6.75
2 atoms oxide of bismuth	ı	•	20
2 atoms water	•	•	2.25
•			90

7. Tetartonitrate of bismuth. When the neutral nitrate of bismuth is digested in water, there remains undissolved a soft white matter in silky needles, usually distinguished by the name of pearl white, or magistry of bismuth. It is said, by Berzelius, to be slightly soluble in water, and to be separable in crystals by heat. According to the analytical experiments of Grouvelle, its constituents are

1 8	atom nitric acid	•	•	6.75
4 8	atoms oxide of bismutl	h	•	40
2 :	atoms water	•	•	2.25
				494

<sup>\*</sup> Ann. de Chim. et de Phys. xix. 141.

<sup>†</sup> Ibid. p. 138.

Class 1.

8. Triscarbonate of bismuth. This salt is obtained when nitrate of bismuth is decomposed by an alkaline carbonate. It is a white tasteless powder, insoluble in water, but soluble with effervescence in nitric acid. Its constituents, by my analysis, are

1 atom carbonic acid	•	•	2.75
3 atoms oxide of bismuth	•	•	30
2 atoms water	•	•	2.25
			35

9. Phosphate of bismuth. When phosphate of soda is mixed with a solution of nitrate of bismuth, containing enough of nitric acid to prevent it from being precipitated by water, a white precipitate falls. When edulcorated and dried without heat, it is a white tasteless powder, insoluble in water, and apparently neutral. 5.22 grains of it when ignited lose 1 grain of moisture. Hence the salt is probably a compound of

1 atom phosphoric acid		•	4.5
1 atom oxide of bismuth	•		10
3 atoms water	•	•	3.375
			17:875

10. Arseniate of bismuth. This salt may be formed by the same process as the last, merely substituting arseniate of soda for phosphate of soda. It is a white powder with a slight shade of yellow. It is tasteless, insoluble in water, and incapable of altering vegetable blues. 19.75 grains of it, by ignition, lose 2.01 grains of water. Hence its constituents seem to be

1 atom arsenic acid	•	•	7.25
1 atom oxide of bismuth	•		10
2 atoms water	•	•	2.25
			19.5

The water is deficient by rather less than 1 d of an atom.

- 11. Borate of bismuth. A white powder insoluble in water.
- 12. Silicate of bismuth. Oxide of bismuth fuses easily with silica into a yellow glass.
- 13. Chromate of bismuth. This salt is obtained when chromate of potash is mixed with acidulated nitrate of bismuth. It is a fine yellow powder, insoluble in water, and not affecting vegetable blues. Its constituents are

l atom chromic acid	•	•	6.5
1 atom oxide of bismuth	•	•	10
<sup>•</sup> 2 atoms water	•	•	2.25
•			18.75

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- 14. Molybdate of bismuth. Obtained by mixing molybdate of potash with nitrate of bismuth. A lemon-yellow powder, soluble in 500 times its weight of water, and in the strong mineral acids.\* Tungstic acid throws down a yellow-brown precipitate from nitrate of bismuth.+
- 15. Oxalate of bismuth. It may be formed by mixing oxalate of ammonia, and nitrate of bismuth. It is a fine white tasteless powder, insoluble in water, and producing no change on vegetable blues. It is anhydrous, and composed of

1 atom oxalic acid	•	•	4.5
1 atom oxide of bismuth	•	•	10
•			14.5

- 16. Acetate of bismuth. Acetic acid has but little action on bismuth; but the acetate of bismuth may be obtained by mixing together the solutions of nitrate of bismuth and acetate of potash. When the mixture is heated, it redissolves the precipitate which had at first formed, and at the same time yields a number of thin talky crystals resembling boracic acid. Morveau, to whom we are indebted for this experiment, has ascertained also, that the addition of acetic acid, deprives nitrate of bismuth of the property of affording a precipitate when diluted with water.‡
- 17. Formate of bismuth. Crystals, easily soluble in water, blackening when heated.
- 18. Tartrate of bismuth. Readily formed by double decomposition. A fine, white, tasteless, insoluble powder. Its constituents are

1 atom tartaric acid	•	. •	8.25
1 atom oxide of bismuth		•	10
5 atoms water	•	•	5.625
			<del></del>
			23.875

19. Succinate of bismuth. Succinic acid does not attack bismuth; but it dissolves its oxide at a boiling temperature, and the solution yields yellow crystalline plates of succinate of

<sup>\*</sup> Richter + Scheele. ‡ Encyc. Method. Chim. i. 10. § Arsvedson.

bismuth. According to Wenzel, the solution of this salt in water does not yield a precipitate with alkalies. It dissolves in nitric acid, and the solution is not precipitated by water.\*

- 20. Benzoate of bismuth. Benzoic acid dissolves the oxide of bismuth with facility; and the solution yields white needle-shaped crystals, which are not altered by exposure to the air, are soluble in water, and very sparingly soluble in alcohol. Sulphuric and muriatic acids decompose this salt, and heat volatilizes its acid.† Hisinger found that benzoate of ammonia throws down a white precipitate when dropt into nitrate of bismuth. This precipitate is somewhat soluble in water.
- 21. Gallate of bismuth. Sublimed gallic acid colours nitrate of bismuth yellow, and a copious yellowish-brown precipitate falls.
- 22. Croconate of bismuth. Croconate of potash when dropt into nitrate of bismuth, throws down a lemon-yellow precipitate soluble in an excess of bismuth salt.
- 23. Pinate of bismuth. May be obtained by precipitating nitrate of bismuth by pinate of potash. It is insoluble in water, but dissolves in ether with the separation of flocks. It is composed of

The salts of bismuth have been examined hitherto in rather a cursory manner.

# SECTION XXX.—SALTS OF SUBOXIDE OF MERCURY.

There is no genus of metallic salts which has been subjected to a longer or more varied examination than this. Mercury was the metal from which the alchymists conceived the greatest hopes, and which they exposed to every possible torture during their researches after the philosopher's stone. The introduction of mercurial salts into medicine occasioned a scrutiny no less varied than obstinate, after the paroxysm of the alchymists was over. The important cures performed by their means, especially in cases of the venereal disease, were early seen by physicians; but the energy with which they acted, and the ravages which they sometimes made on the constitutions of

Wenzel's Verwandtschaft, p. 243.

<sup>†</sup> Trommsdorf, Ann. de Chim. xi. 317.

<sup>‡</sup> L. Gmelin.

<sup>§</sup> Unverdorben, Poggendorf's Annalen, xi. 230.

those who used them, were equally visible. These deleterious Sect. XXX. effects were ascribed to a certain acrid something which was supposed to constitute a component part of mercury. object of chemical physicians was long directed towards discovering a method of removing, neutralizing, or destroying this acrid something, without impairing the good effects of the medicine. Hence the numerous preparations of mercury which were one after another introduced into practice; some of which have, in a great measure, answered the purposes for which they were intended; while the greater number, after continuing fashionable for a time, have gone one after another out of use.

Mercurial salts have lately engaged the attention of philosophical chemists, because, from the peculiar nature of the metal, the changes which take place during their formation are more easily traced. To them we are indebted for the discovery of the composition of sulphuric acid, of metallic oxides, and for the first decisive proofs of the non-existence of phlogiston; to them we owe the discovery of oxygen gas, and perhaps also of nitrous gas.

Mercurial salts are distinguished by the following properties. Characters.

- 1. When strongly heated, they are volatilized and dissipated; and traces of mercury may sometimes be observed.
- 2. Prussiate of potash occasions a whitish precipitate, which becomes yellow when exposed to the air.
  - 3. Hydrosulphuret of potash occasions a black precipitate.
- 4. Muriatic acid, when poured into their solution in water, occasions a white precipitate.
- 5. Gallic acid, or the infusion of nutgalls, occasions an orangeyellow precipitate.
- 6. A plate of copper plunged into a liquid mercurial salt gradually precipitates running mercury.
- This salt may be formed 1. Sulphated suboxide of mercury. by heating one part of mercury in from 1 to  $1\frac{1}{\alpha}$  parts of sulphuric acid. Sulphurous acid is disengaged abundantly. The process is to be stopped when the mercury is converted into a white crystalline powder. When this matter is washed with a little water, to remove the excess of acid, it constitutes a white salt in scales. It has very little taste, reddens vegetable blues, and when heated the colour becomes darker, the salt assumes a silky lustre, and the scaly structure becomes much more conspicuous. 32.725 grains, when heated on the sand bath, lost 1.725 grains of their weight. It has not been rigidly analyzed; but supposing it neutral, the constituents seem to be

1 atom	sulphuric	e acid		•	5
1 atom	suboxide	of me	ercury	7	<b>2</b> 6
$l_{\frac{1}{2}}$ atom	water	•	•	•	1.6875
					32.6875

- 2. Subsulphated suboxide of mercury. When the preceding salt is washed with a great deal of water, it loses a portion of its acid, and is converted into a beautiful yellow powder, which is obviously a subsulphated suboxide.
- 3. Supersulphated suboxide of mercury. This salt may be obtained by dissolving the neutral sulphate in water acidulated with sulphuric acid. Its nature has never been particularly investigated.
- 4. Nitrated suboxide of mercury. When nitric acid is allowed to act upon mercury without the assistance of heat after a certain portion of the mercury has been dissolved, but while uncombined acid and mercury still remain, transparent crystals are deposited, which are nitrated suboxide. These are usually described as cubo-octahedrons; but I have always obtained four-sided prisms. This salt is not sensibly altered by exposure to the air. It has the disagreeable taste which characterizes the soluble mercurial salts. It is soluble in a small portion of water; but when digested in a large portion of that liquid, it is decomposed. But when the liquid is acidulated with nitric acid, the solution is complete. By heat it is decomposed. On burning coals it detonates feebly, or rather burns with flame. Its constituents, by my analysis, are

1 atom nitric acid	•	. 6.75
1 atom suboxide of mercury	•	<b>26</b>
2 atoms water	•	2.25
		35*

This analysis has been since confirmed by Mitcherlich.+

5. Subsesquinitrated suboxide of mercury. When the action of nitric acid upon mercury is continued till the whole nitric acid is saturated, taking care that there be present an excess of mercury, crystals are deposited of another form, according to Mitcherlich, though he has neglected to specify their shape. They are large transparent prisms. They may be dissolved in a little water; but when digested in a large quantity, they

<sup>\*</sup> First Principles, ii. 396.

<sup>†</sup> Ann. de Chim. et de Phys. xxxv. 421.

undergo decomposition. The constituents of this salt, accord- Sect. XXX. ing to the analysis of Mitcherlich, are

1 atom nitric acid 6.75 1 atom suboxide of mercury 39  $1\frac{1}{a}$  atom water 1.6875 47.4375\*

Grouvelle prepared this 6. Dinitrated suboxide of mercury. salt probably by decomposing the nitrated suboxide by water, and found it a compound of

1 atom nitric acid 6.752 atoms suboxide of mercury 52.0058.75+

It is a white powder, which by farther washing becomes yellow, and may, according to Mitcherlich, be deprived of the whole of its acid by repeated washings.

- 7. Hyponitrited suboxide of mercury. This salt may be obtained by boiling an aqueous solution of nitrated suboxide over mercury till the liquid assumes a dark yellow colour, and then evaporating the solution. It is a lemon-yellow salt, very little soluble in water. ±
- 8. Chlorated suboxide of mercury. Chloric acid readily dissolves suboxide of mercury. As the saturation goes on, the chlorate precipitates in the state of yellowish grains. This chlorate has very much the appearance of phosphate of silver. It has a mercurial taste, and dissolves very sparingly in boiling water. When heated, it detonates, oxygen gas is given out, and corrosive sublimate formed.
- 9. Iodated suboxide of mercury. Iodate of potash, when poured into nitrated suboxide, throws down a white precipitate with a pearly lustre, scarcely soluble in water, but soluble in iodic acid.
- 10. Sesquicarbonated suboxide of mercury. This salt is obtained when a solution of nitrated suboxide is precipitated by carbonate of soda. It is a white, tasteless powder, insoluble in water, but converted, according to Proust, into peroxide of mercury by exposure to the air. I found it to be a compound of

II.

<sup>\*</sup> Ann. de Chim. et de Phys. xxxv. 423.

t Mitcherlich.

<sup>§</sup> Vauquelin, Ann. de Chim. xcv. 103. 2 y

<sup>†</sup> Ibid. xix. 139.

1 atom suboxide of mercury . 4.125

30.125\*

11. Phosphated suboxide of mercury. When phosphate of soda is mixed with a solution of nitrated suboxide of mercury, the phosphate precipitates. It is a tasteless, white powder, insoluble in water, nor does it dissolve in water acidulated with phosphoric acid. From 96.2 grains of nitrated suboxide of mercury, I obtained in this way 85.3 grains of phosphate, which lost scarcely any weight when heated as strongly as it would bear without decomposition. Hence its constituents were

85.30+

This is equivalent to

1.12 atom phosphoric acid,

1 atom suboxide of mercury.

It appears from this, that the salt contained a slight excess of phosphoric acid, unless this excess was only apparent, and derived from water which could not be driven off without decomposing the salt.

12. Arseniated suboxide of mercury. When arseniate of soda is poured into a solution of nitrated suboxide, this salt precipitates. It is a gray powder, destitute of taste, and insoluble in water. It loses no weight when heated on the sand bath, and may therefore be considered as anhydrous. Supposing it neutral, its constituents are

- 13. Borated suboxide of mercury. Boracic acid has no action on mercury; but borate of soda, poured into a solution of that metal in nitric acid, occasions a precipitate of borate of mercury in the state of a yellow powder, first described by Monnet.
- 14. Selenited suboxide of mercury. A white insoluble powder, obtained by pouring selenious acid into a protosalt of mercury. When heated it melts, and forms a mass of a deep

<sup>\*</sup> First Principles, ii. 398.

brown colour. When cold, the colour becomes lemon-yellow. Sect. XXX. When more strongly heated, it may be distilled over in amber coloured drops, usually transparent. It is decomposed by potash, and likewise by muriatic acid.\*

15. Chromated suboxide of mercury. This salt precipitates when chromate of potash is mixed with a solution of nitrated suboxide. It is a fine dark red powder, insoluble in water, and destitute of taste. When heated, it loses about 2.8 per cent. of water, which being less than an atom, is probably only hygrometrical. Supposing it anhydrous, its constituents are

- 16. Molybdated suboxide of mercury. Molybdate of potash, when dropped into nitrated suboxide, throws down a yellow precipitate, soluble in about 600 times its weight of water, and decomposed by digestion in nitric acid.
- 17. Tungstated suboxide of mercury. Tungstic acid forms with the suboxide of mercury an insoluble powder, which has not been examined.
- 18. Oxalated suboxide of mercury. This salt is formed when oxalate of ammonia and nitrated suboxide are mixed together. It is a white powder, nearly tasteless, and insoluble in water. When dried in the temperature of 100°, it is a beautiful white powder, which, when placed on the sand bath, gives out a little water, and then explodes with considerable violence. Its constituents seem to be

19. Acetated suboxide of mercury. This salt is precipitated in beautiful silky scales, when solutions of nitrated suboxide and acetate of soda are mixed. It has the disagreeable taste of the mercurial salts, but is the least soluble of all the acetates, requiring about 600 times its weight of water to dissolve it. According to the experiments of Dumas, † it is anhydrous, and composed of

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 342.

<sup>†</sup> Ann. des Mines, xii. 219.

I inferred that it contained four atoms of water; but as I obtained only one of the constituents the inference was drawn from insufficient data.\*

- 20. Lactated suboxide of mercury. Lactic acid dissolves the suboxide of mercury, and forms a light yellow-coloured matter which becomes white by repeated solution and evaporation. It contains an excess of acid, deliquesces in the air, and is partly dissolved in alcohol. But at the same time the salt is decomposed.
- 21. Formated suboxide of mercury. When suboxide of mercury is dissolved in formic acid, the colourless solution, when concentrated, deposites soft, white, four-sided prisms. They are soluble in water, but the solution speedily undergoes decomposition.‡
- 22. Mellated suboxide of mercury. Mellitic acid, when dropt into nitrated suboxide throws down a white precipitate soluble in nitric acid.
- 23. Tartrated suboxide of mercury. This salt is precipitated when tartrate of potash is mixed with a solution of nitrated suboxide. The precipitate, when it first falls, is snow white, but in a few minutes it blackens considerably, and when collected on the filter, washed and dried in the open air, it becomes gray. It has scarcely any taste, and is not sensibly soluble in water. This salt is anhydrous, and composed of

1 atom tartaric acid . . 8.25 1 atom suboxide of mercury . . . 26 34.25

- 24. Vinated suboxide of mercury. Vinic acid gives, with nitrated suboxide, a white precipitate, which blackens when exposed to the light.
- 25. Pyrotartrated suboxide of mercury. Pyrotartrate of potash gives, with nitrated suboxide, a thick white precipitate.
- 26. Citrated suboxide of mercury. Citric acid does not precipitate nitrated suboxide, but it gives a precipitate with acetated suboxide. This salt is a white powder, soluble in nitric acid.
  - \* First Principles, ii. 400.
  - ‡ Göbel. § Klaproth.

† Berzelius, Djurkemien, ii. 438.

|| Walchner. ¶ Rose.

- 27. Malated suboxide of mercury. Pure malic acid does sect. xxx. not precipitate nitrated suboxide; but a white precipitate falls if the malic acid be impure.\*
- 28. Pyromucated suboxide of mercury. A white precipitate falls when pyromucate of potash is mixed with nitrated suboxide of mercury.
- 29. Succinated suboxide of mercury. When succinate of potash is dropt into nitrated suboxide a white precipitate falls, which is insoluble in water.
- 30. Benzoated suboxide of mercury. Benzoic acid, or Benzoate of ammonia, when dropt into nitrated suboxide, throws down a precipitate in white needles, which is insoluble in water.‡
- 31. Camphorated suboxide of mercury may be obtained by double affinity. It is a white powder, which becomes gray when dried, and is scarcely soluble in water.§
- 32. Suberated suboxide of mercury. A white powder, obtained when suberic acid is dropt into nitrated suboxide of mercury.
- 33. Pinated suboxide of mercury. Nitrated suboxide is precipitated by pinate of potash. The salt is in the state of white flocks, soluble in other. When boiled in alcohol they become black.
- 34. Silvated suboxide of mercury is similar to the preceding salt.\*\*
- 35. Carbazotated suboxide of mercury. It may be obtained by mixing boiling solutions of carbazotate of soda and nitrated suboxide. It is deposited in small yellow three-sided prisms. It requires about 2000 times its weight of water to dissolve it.++
- 36. Indigotated suboxide of mercury. It may be obtained by double decomposition, and is an insoluble white powder. It is composed of

37. Sulphonaphthalated suboxide of mercury. Sulphonaphthalic acid dissolves carbonated suboxide of mercury, and forms a salt not quite neutral and crystallizing imperfectly in the air.

\* Braconnot.

+ Gehlen.

‡ Hisinger.

§ Brandes, Schweigger's Jour. xxxviii. 299.

| Ibid. xxxiii. 97.

¶ Unverdorben, Poggendorf's Annalen, xi. 236.

\*\* Ibid. p. 402.

<sup>††</sup> Liebig, Ann. de Chim. et de Phys. xxxv. 85.

<sup>‡‡</sup> Buff, Ibid. xli. 179.

It is white, has a mercurial taste, does not deliquesce, and is

decomposed by heat.\*

38. Sinapated suboxide of mercury. Sinapic acid when dropt into nitrated suboxide of mercury, throws down a white curdy precipitate.+

#### SECTION XXXI. -- SALTS OF OXIDE OF MERCURY.

The salts of oxide of mercury have a considerable analogy to those of suboxide. Some are soluble in water, and the solution is usually transparent and colourless. Those which are insoluble in water are almost all soluble in nitric acid, and the solution is transparent and colourless. We may distinguish the salts of oxide of mercury by the following properties:

Characters.

- 1. A solution of potash dropt into a solution of such salts throws down a yellow precipitate, not soluble in an excess of potash. But if to the liquid we previously add some sal ammoniac, then the potash precipitate is white. The same colour is observable when the liquid contains much uncombined acid.
- 2. Ammonia throws down a white precipitate not soluble in an excess of the reagent.
- 3. Carbonate of potash throws down a reddish-brown precipitate not soluble in an excess of the reagent. Carbonate of ammonia throws down a white precipitate. The same observation applies to oxalate of ammonia and prussiate of potash. The prussiate of potash precipitate, after some time, becomes blue.
- 4. Hydrosulphuret of ammonia, added in very small quantity, produces a *black* precipitate, which, when the liquid is shaken, becomes white, and remains long suspended. When hydrosulphuret of ammonia is added in excess the precipitate is *black*. It is insoluble in ammonia; but dissolves in potash. Sulphuretted hydrogen acts precisely in the same way.
- 5. Iodide of potassium throws down a scarlet-coloured precipitate, and chromate of potash a yellowish-red powder, provided the liquid be not too dilute.
- 6. A plate of copper put into a solution of oxide of copper is soon whitened, being converted into an amalgam.
- 7. When mixed with carbonate of soda and exposed to the action of the blow-pipe, mercury is reduced to the metallic state.

<sup>\*</sup> Faraday, Annals of Philosophy (2d series), xii. 241.

<sup>†</sup> Henry and Garot.

1. Sulphate of mercury. This salt may be formed by boil-sect.XXXI. ing mercury violently, and for a considerable time, in concentrated sulphuric acid. The sulphated suboxide at first formed is gradually changed into sulphate. If we treat in this way 2 parts of mercury and 3 of strong acid, the whole salt formed is sulphate. When prepared in this way I found it in white irregular crystals, strongly reddening litmus paper, and composed of

2. Disulphate of mercury. This salt is obtained when the preceding salt is well washed in hot water. It was known formerly by the name of turpeth mineral. Its specific gravity is 6.444.\* It is soluble in 2000 parts of cold water, and in 600 parts of boiling water. The solution is colourless.+

The name turpeth mineral seems to have been given to this salt by Crollius, who boasted of its medicinal virtues, but kept the preparation a secret. He attempted to moderate the violent action of this substance by a long digestion, but without success. The process for preparing it was afterwards made public. Kunkel published a set of experiments on it in 1700, in his Laboratorium Chymicum. The name turpeth was no doubt given from some resemblance which it was supposed to have, either in its colour or effects, to the root of the convolvulus turpethum, a plant formerly used in medicine. From the analyses of Braamcamp and Siquiera Oliva, it is obvious that the constituents of this salt are

1 atom sulphuric acid	•	•	5
2 atoms oxide of mercury	•	•	<b>27</b>
	,		321

- 3. Bisulphate of mercury. It may be obtained by digesting the sulphate in sulphuric acid. It crystallizes in prisms, and deliquesces in the air. I found it impossible to obtain this salt sufficiently free from adhering sulphuric acid to subject it to a satisfactory analysis.
- 4. Dinitrate of mercury. I obtained this salt in beautiful and transparent rhombic prisms, with angles of about 74° and

<sup>\*</sup> Watson's Chemical Essays, v. 68.

<sup>†</sup> Fourcroy, Ann. de Chim. x. 298.

<sup>‡</sup> Ann. de Chim. liv. 125.

106° (measured by the common goniometer,) from a solution of mercury in a great excess of nitric acid, which had been left long in an open dish. When put into water it is decomposed, red oxide of mercury remaining. The solution of red oxide of mercury in nitric acid by careful evaporation may be obtained in crystals. I found the constituents of this salt 1 atom nitric acid and 2 atoms oxide of mercury. Mitcherlich, who has examined it more lately, says that it contains also two atoms of water. If so, its constituents are

1	atom nitric acid .	•	6.75
2	atoms oxide of mercury		27
2	atoms water .		2.25

36

I did not succeed in preserving these crystals. They became first yellow and then doughy, and lost their appearance.

5. Tetranitrate of mercury. When the preceding salt is washed with a small quantity of water a yellow coloured matter remains, which, according to the analysis of Braamcamp and Siquiera Oliva, is a compound of

Nitric acid	•	•	12
Oxide of mercury	•	•	88
		•	
			100

This approaches very nearly

l atom i	nitric acid	•	•	6.75
A atome	avide of m	APPOINT		5.4

60.75

6. Supernitrate of mercury. When mercury is dissolved in an excess of nitric acid with the assistance of heat, or if red oxide of mercury be dissolved in an excess of nitric acid, this salt is obtained. The solution, according to Proust, may be concentrated till its specific gravity amounts to 3.47. It has a very acrid taste, and stains the cuticle black. By concentration, it deposites dinitrate of mercury, but cannot itself be resolved into regular crystals.

Grouvelle mentions a binitrate of mercury composed of

2 atoms nitric	acid .	•	13.5
1 atom oxide o	of mercury	•	13.5

27\*

<sup>\*</sup> Ann. de Chim. et de Phys. xix. 142.

But he gives no account of its properties or of the means of Sect. XXXI. obtaining it.

- 7. Chlorate of mercury. This salt was first obtained by Mr. Chenevix. It may be formed readily by dissolving oxide of mercury in chloric acid. It crystallizes in needles, is pretty soluble in water, and has a strong taste like that of corrosive sublimate. It always contains an excess of acid. When heated in a glass tube it gives out a great deal of oxygen, a yellow matter remains which appears a mixture of red oxide of mercury, corrosive sublimate, and calomel. The first portion of oxygen is disengaged with rapidity, but the last portion not till the heat is considerably elevated.\*
- 8. Subcarbonate of mercury. It is obtained by mixing solutions of carbonate of soda and nitrated mercury. The precipitate is reddish-brown, it has not been analyzed, but according to Proust, the quantity of carbonic acid which it contains is small.
- 9. Phosphate of mercury. It is a white insoluble powder, obtained by mixing together solutions of nitrated mercury and phosphate of soda. According to the analysis of Braamcamp and Siquiera-Oliva, it is composed of

	Acid	•	•	•	•	28.5
	Oxide	•	•	•	•	71.5
/PL:_ :L			4-4			100.0
I nis is ob	viously equal to a tom p			acid	•	4.5
	1 atom o				•	13.5

10. Arseniate of mercury. This salt is obtained when arseniate of soda is mixed with a solution of corrosive sublimate or of nitrated mercury. It is a yellow precipitate, which is soluble in arsenic acid. When arsenic acid is heated over mercury arsenious acid is sublimed, and the same yellow arseniate formed.

18

11. Selenite of mercury is obtained by saturating selenious acid with oxide of mercury. It is a white powder, nearly insoluble in water. When only a certain portion of oxide is dissolved in the acid, if we filter and evaporate, we obtain large prismatic crystals, striated longitudinally. These are biselenite of mercury. This salt dissolves sparingly in alco-

<sup>\*</sup> Vauquelin, Ann. de Chim. xcv. 107.

- Class I.
- hol. It melts when heated in its water of crystallization. The anhydrous salt does not melt, but sublimes without alteration.\*
- 12. Antimoniate of mercury. When antimoniate of potash is mixed with nitrated mercury or corrosive sublimate an orange-yellow precipitate falls.+
- 13. Tellurate of mercury. A white powder, not soluble in water.
  - 14. Chromate of mercury. A yellow soluble salt.
- 15. Oxalate of mercury. A white powder, obtained by adding oxalate of ammonia to acetate of mercury.
- 16. Acetate of mercury. This salt may be formed by dissolving red oxide of mercury in acetic acid, and boiling the solution on fresh red oxide till the acid is saturated. When the liquid cools it deposites crystals of acetate of mercury, as was first observed by Stromeyer and Garot. These crystals are rectangular tables and plates, having their angles frequently truncated. They are sometimes transparent, and sometimes only translucent. Their lustre is pearly. The taste is sharp and mercurial; the smell that of acetic acid, and the salt reddens vegetable blues. When the crystals are exposed to the air they lose acid, and are converted into a subsalt. When heated the salt melts, acetic acid being given out, and is converted into a white granular mass. Ey a stronger heat it is quite decomposed. According to Vogel, when boiled with sugar it is converted into acetated suboxide of mercury.

At the temperature of 50°, the salt dissolves in 4 times its weight of water; ‡ at 66°, in 2.75 times its weight, and in about its own weight of boiling water. § At 66° it dissolves in 17.8 times its weight of alcohol, of the specific gravity 0.811, but at the same time a portion of yellow subsalt is deposited. HAlcohol and ether are capable of depriving it of the whole of its acid. According to the analysis of Stromeyer, it is composed of

Acetic acid	•	•	•	32.336
Oxide of mercury	•	•	•	67.664
				100
This is obviously				
l atom acetic acid	•	•	•	6.25
1 atom oxide of mo	ercur	y	•	13.5
				19.75
* Berzelius, Ann. de Chim et	de P	hve iv	315	+ Be

<sup>\*</sup> Berzelius, Ann. de Chim. et de Phys. ix. 342.

‡ Garot.

§ Stromeyer.

<sup>†</sup> Berzelius.

| Ibid.

making allowance for a slight excess of acetic acid, which does sect. XXXI. not amount to 30th of an atom.

- 17. Mellate of mercury. Mellitic acid when added to nitrated mercury throws down a white precipitate, which is soluble in water.\*\*
- 18. Tartrate of mercury. Tartaric acid throws down from acetate of mercury a white powder, which is a tartrate of mercury.
- 19. Pyrotartrate of mercury. When pyrotartrate of potash is mixed with a solution of corrosive sublimate no change takes place at first, but in a few minutes the liquid becomes muddy and white. After an interval of 12 hours a brown precipitate is deposited.
- 20. Malate of mercury. When red oxide of mercury is dissolved in malic acid a gummy uncrystallizable salt is obtained, which, when digested in water, is decomposed into a submalate which remains, and a supermalate which dissolves in the liquid.‡
- 21. Succinate of mercury. A white powder, difficultly soluble in water. When succinic acid is digested with the oxide of mercury, it forms with it a shapeless mass containing some crystals, and soluble in water; from which the oxide is precipitated by alkalies and hydrosulphurets. These crystals, I conceive, are bisuccinate of mercury. When succinate of ammonia is dropped into corrosive sublimate an insoluble white precipitate falls, which is succinate of mercury.
- 22. Benzoate of mercury. Benzoic acid dissolves the oxide of mercury, and forms with it a white powder, not altered by exposure to the air. It is insoluble in water, and very sparingly soluble in alcohol. A moderate heat sublimes this salt, and a strong heat decomposes it. It is decomposed by lime, by sulphuric acid, and muriatic acid, and by sulphur.
- 23. Meconate of mercury. When meconic acid is added to corrosive sublimate a precipitate slowly falls.
- 24. Pinate of mercury. Pinate of potash throws down a precipitate from corrosive sublimate. It is yellowish red, fusible when gently heated, and soluble in other.\*\*
- 25. Silvate of mercury. This salt resembles the preceding, and may be obtained by a similar process.++
  - \* Klaproth. † Göbel. ‡ Braconnot.
  - § Wenzel's Verwandtschaft, p. 245.
  - || Trommsdorf, Ann. de Chim. xi. 316.
- ¶ Robiquet.
- \*\* Unverdorben, Poggendorf's Annalen, xi. 234. †† Ibid. p. 402.

- 26. Pyrurate of mercury. Pyrurate of potash throws down a precipitate when dropt into nitrated mercury.\*
- 27. Sulphonaphthalate of mercury. Red oxide of mercury is soluble in sulphonaphthalic acid. The solution when evaporated yields a yellowish deliquescent salt, decomposed by heat, burning, and entirely volatile.†

### SECTION XXXII. - SALTS OF OXIDE OF SILVER.

Several of the acids are capable of oxidizing silver; but it resists the action of the greater number. The nitric dissolves it with great facility; hence it is the nitrate of silver with which we are best acquainted. Most of the other acids form with it compounds scarcely soluble in water. The salts of silver may be easily ascertained by the following properties:

Characters.

- 1. The solutions of the soluble salts of silver are colourless and transparent. The insoluble salts are white, or sometimes yellow or red.
- 2. A solution of potash dropt into a salt of silver, gives a light brown precipitate; carbonate of potash throws down a white precipitate. Both of these precipitates are redissolved when ammonia is added.
- 3. Ammonia produces, when poured into a neutral solution of a salt of silver in very small quantity, a brown precipitate, which dissolves at once when a little more ammonia is added.
- 4. When exposed to the action of the blow-pipe upon charcoal, they are reduced, and a globule of silver obtained.
- 5. Prussiate of potash, when dropped into a solution of a salt of silver, occasions a white precipitate.
  - 6. Hydrosulphuret of potash occasions a black precipitate.
- 7. Muriatic acid or the alkaline muriates occasion a white heavy flaky precipitate resembling curd.
- 8. Gallic acid and the infusion of nutgalls occasion a yellow-ish-brown precipitate, at least in several of the solutions of silver.
- 9. When a plate of copper is put into a solution of silver, this last metal is precipitated in the metallic state, retaining, however, a little of the copper alloyed with it.
- 10. The solution of sulphate of iron precipitates the silver in the metallic state.
  - 1. Sulphate of silver. Sulphuric acid does not act on silver
    - \* Chevallier and Lassaigne, Ann. de Chim. et de Phys. xiii. 161.
  - + Faraday, Annals of Philosophy (2d series), xii. 211.

while cold; but when boiled upon that metal in the state of Sect. XXXII. powder an effervescence is produced, occasioned by the escape of sulphurous acid gas, and the silver is reduced to a white mass soluble in dilute sulphuric acid. This solution is limpid and colourless, and yields on evaporation crystals of sulphate of silver. These crystals are white and brilliant, and have the form of very fine prisms.

This salt, according to Wenzel, requires 87½th parts of water to dissolve it; hence the reason that it is generally precipitated in the state of a white powder when sulphuric acid is dropped into a solution containing silver. It is soluble in nitric acid without decomposition.\* When heated, it melts, and in a red heat is decomposed: the silver is reduced, and sulphurous acid and oxygen gas are disengaged. When exposed to the light it is slowly decomposed.

The easiest mode of obtaining it is to mix together solutions of nitrate of silver and sulphate of soda. It falls in the state of a white powder, which may be dissolved in water and crystallized. It has the peculiarly disagreeable taste which characterizes the soluble salts of silver. It is anhydrous, and composed of

1 atom sulphuric acid	•	•	5
l atom oxide of silver	•	•	14.75
			10.75

2. Sulphite of silver. Sulphurous acid does not attack silver, but it combines readily with its oxide. The sulphite assumes the form of small brilliant white grains. It has an acrid metallic taste. Water dissolves only a very minute portion of it: accordingly sulphurous acid occasions a white precipitate of sulphite in solutions of silver. When exposed to the light, it assumes a brown colour. When strongly heated the silver is reduced, and sulphurous and sulphuric acids exhaled.

This salt may be obtained also by mixing together the solutions of sulphite of ammonia and nitrate of silver; but if too much sulphite of ammonia be added, the salt is redissolved, and a double salt formed, composed of sulphurous acid, oxide of silver, and ammonia. The fixed alkalies are also capable of dissolving the sulphite of silver, and forming with it triple salts.+

3. Hyposulphite of silver. When nitrate of silver is dropped

<sup>\*</sup> Klaproth.

into any hyposulphite sufficiently diluted, a white cloud appears, which is redissolved by agitation; on continuing the addition of nitrate of silver the cloud reappears and aggregates into a dirty gray flaky precipitate, which is hyposulphite of silver. This salt is soluble in water, and has an intensely sweet taste. Its solution is not precipitable by a muriate. When kept it gradually undergoes decomposition, and is at last converted into sulphuret of silver.\*

4. Hyposulphate of silver. This salt is easily formed by dissolving carbonate of silver in hyposulphuric acid. When the solution is properly concentrated, it deposites beautiful transparent crystals of hyposulphate of silver. They are eightsided prisms terminated by four-sided pyramids, which have been described and figured by M. Heeren.† These crystals at 60° are soluble in twice their weight of water. They are but little altered by exposure to the air; but when heated they are converted into a gray powder, which is soluble in boiling water, except a small portion of sulphate of silver. From the analysis of Heeren, the crystals are composed of

J	atom hyposulphuric acid		• -	9
1	atom oxide of silver	•	•	14.75
2	atoms water	•	•	2.25
				26t

5. Nitrate of silver. Nitric acid attacks silver with considerable violence, and dissolves about half its weight of it. The effervescence is occasioned by the disengagement of nitrous gas. The acid employed must be pure; if it contains any muriatic acid, as is always the case with the nitric acid of commerce, a white insoluble chloride of silver falls to the bottom of the vessel. If the silver contain gold, that metal is also precipitated in the form of a black or very deep purple powder.

The solution is limpid and colourless, exceedingly heavy, and caustic. It gives the skin, hair, and almost all animal substances, an indelible black colour. Hence it is often used to dye hair, &c. When evaporated till a pellicle begins to form on its surface, it deposites, on cooling, transparent crystals of nitrate of silver. These crystals are brilliant and very irregular; sometimes assuming the form of six-sided, sometimes

<sup>\*</sup> Herschell, Edin. Phil. Jour. i. 26. † Poggendorf's Annalen, vii. 191. † Ibid.

of four-sided, and sometimes of three-sided, thin plates. But Sect-XXXII. by slow crystallization the salt may be obtained in right rhombic prisms, very short, and two of the lateral faces are usually broader than the other two, so as to make the base of the prism not a rhomb but-a rhomboid. The inclination of the lateral faces of the prism is 129° 31', according to the measurements of Mr. Brooke.\* The acute terminal angles of the prism are very often replaced by two planes, which sometimes become so large, as to obliterate almost the lateral faces of the prism.

The taste of this salt is intensely bitter and metallic, and it is usually employed as a corrosive substance, under the name of lunar caustic. It is soluble in its own weight of cold, and in half its weight of hot water. From the solution the silver is thrown down in the metallic state by a great number of bodies. It may be sufficient to name hydrogen, sulphurous acid, sulphate of iron, protochloride of tin, carbon, phosphorus, and volatile oils. All the metals placed before it in the family of easily fusible metals, described in the first volume of this work (p. 543), throw it down in the metallic state, and so do iron and arsenic, and probably also antimony.

Nitrate of silver is soluble in four times its weight of boiling alcohol. When heated, it readily melts, swells up, and then remains liquid. When allowed to cool, it forms a gray-coloured mass, crystallized internally in needles. In that state it is cast in moulds by apothecaries, and formed into small cylinders, often employed by surgeons under the names of lapis infernalis and lunar caustic, to open ulcers and destroy fungous excrescences. Its specific gravity is 3.521.

When this salt is exposed to a red heat, as when it is put upon burning coals, it detonates, and the silver remains pure, attached to the surface of the coal. The same reduction takes place when the salt is distilled in a retort, and nitrous gas, oxygen gas, and azotic gas are disengaged.

This salt, both in crystals and after being melted, has the property of fulminating violently when mixed with phosphorus, and struck smartly with a hammer. This was first observed by Brugnatelli. To the same ingenious chemist we are indebted for the two following facts. When three grains of sulphur and nine grains of nitrate of silver, mixed together, are struck with a cold hammer, the sulphur inflames, but no detonation takes place; whereas if the hammer be hot, the

<sup>\*</sup> Annals of Philosophy (2d series), vii. 162.

mixture detonates, and the silver is reduced. If charcoal be substituted for sulphur, only a faint detonation is heard though the hammer be hot.\*

It is anhydrous, and composed of

21.5

6. Hyponitrite of silver. This salt may be obtained by the following process:—Put a quantity of pure powder of silver into a solution of nitric acid already saturated with silver, and boil the mixture for an hour after nitrous gas has ceased to be evolved; then draw off the clear liquor with a bulbed siphon. The solution is of a pale yellow colour, and it may be concentrated much more than the solution of nitrate, as the nitrite which it affords is much more soluble. When it is in the proportion of 240 to 100 of water, it is still far enough from crystallizing, and sometimes it remains fluid for several days; but if it be poured into a phial, it congeals so suddenly, that the last portions from the mouth of the retort become solid like icicles from the eaves of a house, and a great deal of heat is evolved. It is difficult to bring it to a regular crystallization, because it has a much greater tendency to congeal than to separate into crystals. If it congeal, it cannot be redissolved without the separation of a yellow powder, which is a subnitrite of silver. Hence it appears, that the portion dissolved takes a portion of acid from this yellow powder.

When the solution of hyponitrite of silver is kept in the open air, it soon absorbs oxygen, loses its colour, and deposites crystals of nitrate. The same change is produced immediately by the addition of nitric acid. Hence a few drops of that acid occasion the immediate deposition of large scales of nitrate.

When the solution of hyponitrite of silver is mixed with the infusion of litmus, a blue lake precipitates. Nitrate produces no effect upon this infusion. From the solution of cochineal the hyponitrite throws down a deep violet lake; the nitrate produces a scarlet powder. When the nitrate is dropped into sulphate of indigo, no change is produced; the hyponitrite instantly deprives it of colour, while the silver is reduced. Ammonia precipitates a black powder from the hyponitrite of silver. This black powder is silver reduced. What is dis-

solved by the ammonia is in the state of nitrate. Pure potash sect. XXXII. throws down a brown precipitate, as it does from nitrate. Alcohol acts on hyponitrite of silver precisely as water does. A portion of subnitrite precipitates, and a supernitrite is dissolved. If the alcoholic solution be distilled, it leaves behind a portion of nitrite and of silver reduced. When a little hyponitrite of silver is dropped into boiling water, it is decomposed, a portion of the silver is reduced, and precipitated in the state of a black powder, and the rest of the salt is converted into nitrate.

When the hyponitrite of silver is concentrated in a retort, it grows thick, gives out a little nitrous gas, enters into fusion, and affords a yellow sublimate which lines the sides of the retort. If the melted mass be dissolved, a yellow powder mixed with a little reduced silver precipitates.\*

7. Chlorate of silver. This salt was discovered by Mr. Chenevix. It may be formed by boiling phosphate of silver in chlorate of alumina, or by dissolving oxide of silver in chloric acid. It is soluble in about two parts of warm water; but as the solution cools, it crystallizes in small rhomboids, opaque and dull, like nitrate of lead or barytes. It is soluble in alcohol. Muriatic acid decomposes it, as does nitric, and even acetic acid. The silver is thrown down from its solution by the addition of chlorine.

When this salt is exposed to a moderate heat, it melts, oxygen is given out, and chloride of silver remains behind. When mixed with half its weight of sulphur, and struck slightly, it detonates with prodigious violence. The flash is white and vivid, and accompanied by a sharp and quick noise, and the silver is reduced and volatilized.

- 8. Iodate of silver. When iodic acid is mixed with a solution of nitrate of silver, a white precipitate falls, soluble in ammonia.
- 9. Carbonate of silver. This salt precipitates when an alkaline carbonate is mixed with a solution of nitrate of silver. It is a white insoluble powder, gradually contracting a slight shade of blue. It dissolves in nitric acid with effervescence, owing to the escape of carbonic acid gas. It is anhydrous, and composed of

<sup>\*</sup> Proust, Nicholson's Jour. xv. 376.

<sup>†</sup> Chenevix on the Oxygenized and Hyperoxygenized Muriatic acids, p. 39.

<sup>‡</sup> Gay Lussac.

1 atom carbonic acid . 2.75
1 atom oxide of silver . 14.75

10. Subsesquiphosphate of silver. When phosphate of ammonia is poured into a solution of nitrate of silver, a yellow powder precipitates, which after edulcoration and drying is insoluble in water, but not quite destitute of taste. Its specific gravity is 7.321.\* It is anhydrous. It may be exposed to ignition without fusing, but it may be melted before the blowpipe. At an incipient red heat it becomes reddish-brown, but recovers its yellow colour on cooling. If kept long in fusion

more fusible, and gives it a paler colour.

The mean of three very careful analyses of this salt by Stromeyer, give its constituents as follows:

it is partially converted into pyrophosphate, which renders it

Phosphoric acid . . . 16.545 Oxide of silver . . . 83.455

This is equivalent to

atom phosphoric acid,

1.538 atom of silver.

Berzelius's analysis of the same salt gives its composition

atom phosphoric acid,

1.486 atom oxide of silver.

While my analysis of the same salt gives

atom phosphoric acid,

1.471 atom oxide of silver.

The mean of the three gives us

atom phosphoric acid,

1.4983 atom oxide of silver.

This differs by little more than 9100th part from

1 atom phosphoric acid . 4.5  $1\frac{1}{2}$  atom oxide of silver . 22.125

26.625

which is undoubtedly the true constitution of the salt.

11. Pyrophosphate of silver. When pyrophosphate of soda is mixed with a solution of nitrate of silver, the precipitate which falls is white, as was first observed by Mr. Clarke.

<sup>\*</sup> Stromeyer, Ann. de Chim. et de Phys. xliii. 367. † Ibid. p. 374.

This precipitate is much more bulky than the preceding. At sect. XXXII. first it contains water, which it abandons on drying, and becomes anhydrous. Its specific gravity is only 5.306. When heated, it fuses without alteration, at a temperature below ignition, into a dark brown liquid, which on cooling concretes into a white saline mass, crystallized in needles. When heat is first applied, it assumes a yellowish-brown colour, and when cold, still retains a slight shade of that colour. Like the preceding salt, it is insoluble in water, and is not altered when boiled with water. It dissolves readily in nitric acid, and ammonia throws it down unaltered from its solution. But if we heat the nitrous solution, ammonia throws down from it the yellow phosphate of silver.

Phosphoric acid has a stronger affinity for bases than pyrophosphoric acid. Hence if we boil pyrophosphate of silver with phosphate of soda, a double decomposition takes place, pyrophosphate of soda and yellow phosphate of silver being formed.

The mean of three analyses of this salt by Stromeyer, gives its constituents as follows:

		100.00*
Oxide of silver .	•	75·39 ———
Pyrophosphoric acid	•	24.61

This is equivalent to

1.07 atom pyrophosphoric acid,

l atom oxide of silver.

Hence it is probable that the salt is a compound of

1 atom pyrophosphoric acid . 4.5 l atom oxide of silver . 14.75

19.25

The salt is neutral, and, of course, contains half an atom more of acid than the preceding. This explains its greater fusibility. Though no satisfactory explanation of the cause of the difference between phosphoric acid and pyrophosphoric acid can be at present assigned.

12. Subsesquiarseniate of silver. When solutions of nitrate of silver and arseniate of silver are mixed together, a flesh-coloured precipitate falls in large flocks, while the liquid becomes acid. This precipitate is nearly tasteless, and insoluble

<sup>\*</sup> Stromeyer, Ann. de Chim. et de Phys. xliii. 374.

in water. When dried it has a reddish-brown colour. When heated to redness it becomes nearly black, and 34.4 grains of it when thus treated lose 0.5 grain of moisture. Hence, it is obvious that the salt is anhydrous. By a synthetical experiment, I\* found it composed of

This is equivalent to

1 atom arsenic acid, 1.492 atom oxide of silver.

From this, there can be no doubt that the true constitution of the salt is

1 atom arsenic acid . . 7.25  $1\frac{1}{2}$  atom oxide of silver . . 22.125 29.375

13. Arsenite of silver. This salt has been examined by Dr. Marcet, in consequence of his application of it as a test for the discovery of arsenious acid.† It may be obtained by dropping nitrate of silver into a solution containing arsenious acid. An orpiment yellow precipitate appears, which is the salt in question. After some time it becomes brown, and this is the colour which it retains when dry. It is insoluble in water, but dissolves readily in diluted nitric acid. If an excess of ammonia be added just after its formation, it is redissolved. But the dry salt is insoluble in ammonia. When heated in a glass tube a white smoke evaporates, which condenses on the sides of the tube in minute octahedral crystals of arsenious acid, while a dark-brown mass remains, which is an arsenite. Before the blow-pipe upon platinum, and still better upon charcoal, the silver is reduced, and the arsenic dissipitated.‡

14. Borate of silver. Boracic acid has no action on silver whatever, but the borate may be formed by pouring a solution of borax into liquid nitrate of silver. The salt falls to the bottom in the form of an insoluble white powder, which has not been examined.

15. Selenite of silver. This salt is precipitated in the state of a white powder, by dropping selenious acid into a solution

<sup>\*</sup> First Principles, ii. 410.

<sup>†</sup> Mr. Hume first proposed nitrate of silver as a mode of detecting small quantities of arsenious acid. But the use of this test was materially improved by the experiments of Dr. Marcet and Dr. Paris.

<sup>‡</sup> Annals of Philosophy, iii. 236.

of nitrate of silver. Boiling water dissolves a little of it. It sect. XXXII. dissolves completely in boiling nitric acid, but is precipitated again when the acid is diluted with water. If a boiling solution of this salt in nitric acid be mixed with boiling water, the seleniate falls down in needles as the solution cools. This salt is not blackened by exposure to the light. When heated it melts, and becomes transparent like chloride of silver. On cooling, it is converted into a white, opaque, friable mass, the fracture of which exhibits a crystallized texture. When strongly heated and exposed to a current of air, selenious acid and oxygen gas are disengaged, and it becomes covered with a pellicle of metallic silver. This salt, according to Berzelius, is composed of

Selenious acid . . . 100 Oxide of silver . . . 205.75\*

This approaches pretty nearly to

21.75

- 16. Antimoniate of silver. A white powder, insoluble in water.†
- 17. Tellurate of silver. Tellurate of potash precipitates nitrate of silver white.
- 18. Chromate of silver. This salt is easily obtained by mixing together solutions of nitrate of silver and chromate of potash. It falls in the state of a dark-red powder, which is insoluble in water, and not altered by exposure to the air. It is anhydrous, and composed of

1 atom chromic acid . . . 6.5 1 atom oxide of silver . . . 14.75

21.25‡

- 19. Molybdate of silver. When molybdic acid is added to a nitrate of silver, a white flaky precipitate falls.§
- 20. Tungstate of silver. A white powder, not soluble in water.
  - 21. Columbate of silver. A white insoluble powder.
- 22. Oxalate of silver. This salt is easily obtained by mixing together solutions of nitrate of silver and oxalate of ammonia. It falls down in the state of a very fine and white pow-
  - \* Ann. de Chim. et de Phys. ix. 343.

+ Berzelius.

† First Principles, ii. 412.

§ Scheele, i. 146.

der, very different in appearance from chloride of silver. It is scarcely soluble in water, and when heated is very easily blackened. It is soluble in nitric acid. This salt is anhydrous, and composed of

23. Acetate of silver. Acetic acid has no action whatever on silver, but it readily dissolves its oxide, and forms with it acetate of silver. The salt may be formed easily by putting acetate of potash into a solution of nitrate of silver, or by saturating hot acetic acid with the oxide of silver. On cooling, the solution yields, according to Margraff, small needle-form crystals of an acrid metallic taste, and easily dissolved in water.\* When heated, it swells up, the acid is dissipated, and the oxide of silver remains behind.

The crystals have a silky lustre, are white, and consist of long slender four-sided prisms. The salt is very light, and requires 100 times its weight of water to dissolve it. It is anhydrous, and composed of

1 atom acetic acid	•	•	6.25
1 atom oxide of silver	•		14.75
			21

I obtained by actual experiment

1 atom acetic acid, 1.006 atom oxide of silver.+

Dumas has analyzed the salt since, and has come nearer the truth, having obtained as the constituents

atom acetic acid,1.004 atom oxide of silver.;

24. Lactate of silver. This salt is obtained by dissolving carbonate of silver in lactic acid. The solution has a greenish-yellow colour, and an unpleasant taste of verdigris. When evaporated in a very flat dish, it dries into a greenish-yellow varnish, with surface splendent like that of a mirror. When evaporated in a deep dish, it becomes brown from the reduc-

<sup>\*</sup> Opusc. i. 106. This was denied by Monnet, but found accurate by Kirwan. The saturated solution, filtered while hot, yielded him very speedily acicular crystals. He supposes that Monnet failed by evaporating the solution.—Kirwan on Mineral Waters, p. 81.

<sup>†</sup> First Principles, ii. 413. ‡ Ann. des Mines, xii. 219.

tion of part of the silver. Even in the yellow polished matter a portion of the silver is reduced, as becomes evident by dissolving the salt in water.\* According to Braconnot, lactic acid, from vegetables, readily dissolves oxide of silver when assisted by the application of heat. By evaporation, silky needle-form crystals are formed, collected together in spheres, so that the whole liquid appears coagulated. When dried, it has a fine white colour, but becomes red by exposure to the light. It is soluble at the temperature of 73° in 20 times its weight of water. When heated it melts, swells, becomes brown, catches fire, and leaves metallic silver.†

- 25. Formate of silver. Translucent rhomboidal crystals, easily soluble in water, but insoluble in alcohol. When heated they blacken, and are decomposed.
- 26. Mellate of silver. Mellate of ammonia when dropped into nitrate of silver throws down mellate of silver. It is a white powder, always cohering together, and anhydrous. When heated, it is decomposed with a hissing noise, and the silver is reduced.
- 27. Tartrate of silver. Tartaric acid does not attack silver, but tartar dissolves its oxide, and forms with it a saline mass, which becomes black by exposure to the air. Tartaric acid does not occasion a precipitate in liquid nitrate of silver. When solutions of nitrate of silver and tartrate of potash are mixed together, a fine white powder falls. If we raise the temperature of the liquid a very little, the colour of the precipitate becomes dark-brown. Indeed this change of colour takes place spontaneously if the powder be allowed to remain for 24 hours in contact with the liquid from which it was thrown down. This salt is anhydrous, and composed of

1 atom tartaric acid 1 atom oxide of silver	•	•	8·25 14·75

- 28. Pyrotartrate of silver. Pyrotartrate of potash occasions a precipitate when mixed with nitrate of silver. This precipitate is white, but acquires a bluish tinge when exposed to the light.¶
  - 29. Citrate of silver. Silver is not attacked by the citric

¶ Göbel.

<sup>\*</sup> Berzelius, Djurkemien, ii. 438.

<sup>†</sup> Braconnot, Ann. de Chim. lxxxvi. 92.

<sup>‡</sup> Arfvedson. § Wöhler.

<sup>||</sup> Wenzel's Verwand. p. 218.

acid: but its oxide combines with it, and forms with it a salt insoluble in water, of a harsh metallic taste, which blackens when exposed to the light, and yields, when distilled, acetic acid, while the silver is revived. This salt is decomposed by nitric acid. According to Vauquelin, to whom we are indebted for these facts, it is composed of

36 acid 64 oxide of silver

100\*

# This is obviously

1 atom citric acid	•	•	<b>7·2</b> 5
1 atom oxide of silver	•	•	14.75
			<del></del>
			22

- 30. Malate of silver. Malic acid dissolves oxide of silver, and forms a gum like salt not capable of crystallizing. But the bimalate readily yields crystals when a hot solution is concentrated.†
- 31. Fungate of silver. Fungic acid does not decompose nitrate of silver; but a precipitate is thrown down by fungate of potash.
- 32. Mucate of silver. Mucic acid occasions a white precipitate when dropped into nitrate of silver.
- 33. Pyromucate of silver. When the solution of oxide of silver in pyromucic acid is concentrated, it becomes brown, and deposites the salt in small white scales.
- 34. Succinate of silver. The succinic acid does not act on silver, but it dissolves its oxide, and forms with it a salt which crystallizes in thin oblong radiated prisms.¶
- 35. Benzoate of silver. Benzoic acid does not attack silver, but it dissolves its oxide, and forms with it a salt easily soluble in water, but in a very small proportion in alcohol. It does not deliquesce in the air; but when exposed to the rays of the sun, it becomes brown. Heat volatilizes the acid and revives the silver.\*\*
- 36. Meconate of silver. Meconic acid throws down nitrate of silver in the state of a white powder.++

<sup>\*</sup> Fourcroy, vii. 209. + Braconnot. + Ibid. \$ Scheele, ii. 80.

Labillardiere. ¶ Wenzel's Verwand. p. 245.

<sup>\*\*</sup> Trommsdorf, Ann. de Chim. xi. 313. ++ John.

- 37. Boletate of silver. When boletic acid is dropped into Sect. XXXII. nitrate of silver, a precipitate falls easily soluble in nitric acid.\*
- 38. Camphorate of silver. When camphorate of potash is mixed with nitrate of silver, a white precipitate falls, which becomes blue when exposed to the light. When heated it melts and is decomposed, leaving metallic silver. Its constituents, according to the analysis of Brandes, are

Camphoric acid	•	•	<b>45</b> ·8 <b>45</b>
Oxide of silver	•	•	54.155
			•
			100†

39. Suberate of silver. When nitrate of silver and suberate of ammonia are mixed, a white powder falls, composed, according to Brandes, of

Suberic acid .	•	•	45.455
Oxide of silver	•	•	54.545
			<del></del>
			100

In the light it becomes violet, especially if moist. When heated it melts, becomes first yellow, then black, is decomposed, and leaves silver. It is but little soluble in water.‡

- 40. Pinate of silver. Obtained by mixing together solutions of pinate of potash and nitrate of silver. A yellow powder, which melts when rather strongly heated. It blackens when exposed to the sun. It is insoluble in water, and very little soluble in absolute alcohol. It dissolves readily in ether and in oil of turpentine.§
- 41. Silvate of silver. It may be prepared by a process similar to the preparation of the preceding salt. It is soluble in 15 times its weight of cold absolute alcohol, and in a still smaller quantity of the same alcohol when hot. Has so great an affinity for ether that it will separate it from water. When the alcoholic solution is left to spontaneous evaporation, the salt crystallizes in small grains.
- 42. Carbazotate of silver. Carbazotic acid dissolves oxide of silver with facility, when heated with it in water. By gentle evaporation the solution yields crystals in very fine needles, having the lustre of gold, and grouped in stars. The salt is

<sup>\*</sup> Braconnot. † Schweigger's Jour. xxxviii. 298.

<sup>†</sup> Brandes, ibid. xxxiii. 94.

<sup>§</sup> Unverdorben, Poggendorf's Annalen, xi. 238.

<sup>||</sup> Ibid. p. 401.

very soluble in water. When heated it melts, but does not detonate.\*

- 43. Indigotate of silver. This salt is very little soluble in cold water. It crystallizes in small needles, having a light red colour.†
- 44. Sulphonaphthalate of silver. Moist carbonate of silver dissolves readily in sulphonaphthalic acid. The solution, when evaporated, yields a splendid white salt in crystals, not altered by exposure to the air. When heated it burns with flame, and leaves pure silver. When the solution of the salt is boiled for some time, a black insoluble matter is thrown down, and a solution obtained, which by evaporation, gives abundance of yellow crystals.‡

#### SECTION XXXIII. - SALTS OF PEROXIDE OF GOLD.

Oxide of gold differs from the saline bases hitherto treated of, in this respect, that it seems to possess properties rather analogous to those of acids than of bases. We can form combinations of it with the alkalies and earthy bodies; but no combination with an acid capable of crystallizing. The only solution of gold that we have it in our power to form is the chloride, which is yellow, and very acrid. The action of reagents upon this solution is as follows:

Characters.

- 1. Potash added in excess produces at first no change; but by degrees the liquid assumes a greenish colour, and a little black matter falls down.
- 2. Ammonia throws down a yellow precipitate, which is fulminating gold, and which is redissolved by adding the ammonia in great excess.
- 3. Carbonate of potash produces no precipitate; but carbonate of ammonia effervesces with the liquid, and throws down a yellow precipitate.
  - 4. Prussiate of potash strikes an emerald-green colour.
  - 5. Nitrated suboxide of mercury occasions a black precipitate.
- 6. Sulphate of iron throws down the gold in the metallic state. So does oxalic acid, but not so completely.
- 7. Protochloride of tin strikes a purple colour with very dilute solutions, and throws down a brown coloured precipitate when the solution is more concentrated.
  - 8. Hydrosulphuret of ammonia throws down a dark brown

<sup>\*</sup> Liebig, Ann. de Chim. et de Phys. xxxv. 84. + Buff, ibid. xli. 182.

<sup>‡</sup> Faraday, Annals of Philosophy (2d series), xii. 210.

precipitate, which is redissolved on adding an excess of the Sect. XXXIV. hydrosulphuret.

- 1. Sulphate of gold. Oxide of gold dissolves in sulphuric acid; but it does not neutralize the acid. The solution is yellow, and very acid. When we dilute it with water, or heat it, the gold falls down in the metallic state.\*
- 2. Nitrate of gold. Nitric acid attacks the oxide of gold only when concentrated. The solution has a brown colour, and always contains a great excess of acid. When diluted with water, the oxide of gold precipitates mixed with gold. There appears to be but little affinity between nitric acid and oxide of gold. Hence no doubt the reason why this acid does not dissolve gold in the metallic state.† When the solution is heated, the gold is precipitated in the metallic state.
- 3. Iodate of gold. Iodic acid and iodate of potash throw down from chloride of gold, a yellow precipitate, which is soluble in water.
- 4. Arseniate of gold. Arseniate of soda throws down a yellow precipitate, when added to a solution of chloride of gold.
- 5. Molybdate of gold. Molybdate of potash throws down from chloride of gold an orpiment yellow precipitate, which is soluble in muriatic acid, nitric acid, and seemingly also in water.§
- 6. Acetate of gold. Concentrated acetic acid dissolves oxide of gold, but it is soon deposited again in the metallic state.
- 7. Benzoate of gold. When oxide of gold obtained by means of potash is dissolved in benzoic acid, small irregular crystals are obtained which are not altered by exposure to the air. They are difficultly soluble in water, and not at all in alcohol.

Benzoate of potash does not precipitate chloride of gold.

8. Pinate of gold. Chloride of gold is precipitated by pinic acid. The precipitate is yellow. When exposed to the light it becomes violet, and at last black. When boiled in water it becomes black, and the gold is reduced.

#### SECTION XXXIV. -- SALTS OF PEROXIDE OF PLATINUM.

The investigation of the salts of platinum has not made much greater progress than of those of gold, and for the very same

<sup>\*</sup> Pelletier. + Vauquelin, Ann. de Chim. lxxvii. 332. ‡ Pleischl.

<sup>§</sup> Richter. || Tromsdorf.

<sup>¶</sup> Unverdorben, Poggendorf's Annalen, xi. 236.

reason. Almost the only solution of platinum which we can procure is the chloride. The characters by which a solution of platinum may be distinguished are the following:

Characters.

- 1. The chloride has a fine reddish-brown colour, and is transparent.
- 2. Potash occasions a yellow precipitate, which is not sensibly soluble in acids; but it dissolves when heated in an excess of potash, and does not again precipitate when the liquid cools.
- 3. With ammonia the phenomena are exactly the same as with potash.
- 4. Carbonates of potash and of ammonia produce similar effects. But the precipitates are not re-dissolved when heated in an excess of the alkaline carbonates.
- 5. Neither soda nor its carbonates throw down any precipitate.
- 6. Nitrated suboxide of mercury throws down a yellowish red precipitate.
- 7. Neither oxalic acid nor phosphate of soda occasion any precipitate.
- 8. Sulphuretted hydrogen changes the colour to brown, and by degrees a brown precipitate falls, which becomes gradually black. Hydrosulphuret of ammonia produces the same effect; but the precipitate is re-dissolved when an excess of the hydrosulphuret is added.
- 9. A plate of zinc precipitates platinum from its solutions in the state of a black metallic powder.
- 1. Sulphated peroxide of platinum. This salt is formed when moist sulphuret of platinum is exposed to the air, or still better when it is heated with nitric acid.

Sulphated peroxide of platinum, thus formed, has a very dark-brown colour, approaching black. It is obtained in the form of a porous crust, similar to the carbonaceous matter left when sugar is decomposed by heat. It is very brittle and easily reduced to powder. Its lustre is somewhat similar to that of crystallized blende. Its taste is acid and metallic, with some degree of causticity. It slightly reddens litmus paper. It is very deliquescent, and of course very soluble in water. It is soluble in alcohol, ether, muriatic acid, nitric acid, and phosphoric acid. The alkalies form triple compounds with it. Its solution in water has a dark-brown colour of great intensity. Sal ammoniac does not occasion a precipitate when dropped into it; but, if the solution be boiled to dryness, the ammoniomuriate is formed. The sulphuric acid cannot be separated

from this salt by any of the usual methods, in consequence of sect. XXXIV. the disposition which the salt has of entering into triple compounds. When heated to redness, it is entirely decomposed, and metallic platinum obtained. Oxygen gas, and some sulphurous acid gas is obtained, and a liquid similar to the smoking sulphuric acid of the Germans. From the analysis of Mr. E. Davy, it appears that this sulphate is composed of

This is obviously equivalent to

1 atom sulphuric acid	5
1 atom peroxide of platinum	14
_	
	19

- 2. Nitrated peroxide of platinum. This salt may be obtained by mixing sulphated peroxide of platinum and nitrate of barytes in the atomic proportions, and filtering. If saltpetre be added to chloride of platinum, as long as potash-chloride of platinum precipitates, a dark-brown liquid will remain, which after evaporation leaves a mass which is partially soluble in water, leaving a subsalt.\* The properties of these salts are still unknown.
- 3. Iodated peroxide of platinum. Iodic acid gives with chloride of platinum a yellow precipitate, somewhat soluble in water.
- 4. Arseniated peroxide of platinum. Arseniate of soda, when added to nitrated peroxide of platinum, throws down a light-brown precipitate, soluble in nitric acid.
- 5. Chromated peroxide of platinum. Chromate of potash, when dropt into chloride of platinum, throws down a dark-red precipitate, which becomes tile-red when dried.
- 6. Oxalated peroxide of platinum. When the precipitate thrown down from chloride of platinum by soda is digested in oxalic acid, a yellow-coloured solution is obtained, which yields yellow crystals.
- 7. Benzoated peroxide of platinum. Obtained by dissolving oxide of platinum in the acid. Yellow stelliform crystals are obtained, which are not altered by exposure to the air, diffi-

<sup>\*</sup> Berzelius. † Pleischl.

cultly soluble in water, and not at all in alcohol.\* Benzoate of ammonia does not precipitate solutions of platinum.+

8. Camphorated peroxide of platinum. Camphorate of soda, when mixed with chloride of platinum, throws down a white precipitate, somewhat soluble in water.

## SECTION XXXV. -- SALTS OF PROTOXIDE OF PLATINUM.

This genus of salts is almost quite unknown, owing chiefly to the difficulty of procuring protoxide of platinum in a separate state. It is probable that their saline characters would be more decided than those of the salts described in the last section. The tests of platinum described at the beginning of the last section, would probably apply also to the salts of the protoxide. But I have not myself made any experiments on the subject.

- 1. Sulphate of platinum. When a mixture of subchloride of platinum and sulphuric acid is exposed to the continued action of heat till it no longer precipitates nitrate of silver, and then evaporated to dryness, we obtain a matter which deliquesces in the air, and which dissolved in a little water is black, but in a great deal of water it forms a yellowish-green liquid. When potash or soda is added to this liquid, it becomes at first darker, but in a few days it loses its colour, the platinum precipitating in the state of a hydrated protoxide.
- 2. Nitrate of platinum. Hydrated protoxide of platinum dissolves in dilute nitric acid with a greenish-brown colour. When the solution is evaporated nearly to dryness, it is almost black. But this salt is mixed with a good deal of nitrated peroxide of platinum.
- 3. Acetate of platinum. This salt may be obtained by dissolving moist hydrated protoxide of platinum in acetic acid. The solution has a greenish colour. It may be dried into a dark greenish brown mass, which may be again dissolved in water, except a little protoxide which is left behind undissolved.

### SECTION XXXVI. -- SALTS OF OXIDE OF PALLADIUM.

The great difficulty of procuring palladium, has hitherto prevented chemists from investigating its salts. Hence this

<sup>\*</sup> Trommsdorf.

<sup>‡</sup> Brandes, Schweigger's Jour. xxxviii. 299.

<sup>|</sup> Berzelius.

<sup>†</sup> Hisinger.

genus of salts is at present very imperfectly known. The Sect. XXXVI. characters of these salts are as follows:

- 1. They are almost all soluble in water, and the colour of Characters. the solution is a fine red.
- 2. Prussiate of potash occasions an olive, or rather a dirty yellowish-brown precipitate.
- 3. Hydrosulphuret of potash occasions a blackish-brown precipitate.
  - 4. The alkalies occasion an orange-coloured precipitate.
- 5. Mercury and sulphate of iron throw down the palladium in the metallic state.
- 6: Protochloride of tin renders the solution opaque by throwing down a brown precipitate; but if the solution be sufficiently diluted, it assumes a fine emerald-green colour.

Neither nitrate of potash nor sal ammoniac occasion any precipitate.

- 1. Sulphate of palladium. Sulphurie acid boiled upon palladium acquires a beautiful red colour, and dissolves a portion of the substance; but the action of this acid is not very powerful.\* It is a red incrystallizable matter which dissolves in water.
- 2. Disulphate of palladium. When sulphuret of palladium is exposed to a low red heat in the air, it is converted into this salt. It is a brownish red matter, easily soluble in muriatic acid, and by a stronger heat reduced to metallic palladium.
- 3. Nitrate of palladium. When palladium is put into a strong colourless nitric acid, the liquid gradually acquires a red colour; but the action of the acid is extremely slow, no nitrous gas whatever being extricated. This fact hitherto unique in the history of the action of metals on nitric acid, explains in some measure the slowness of the action of the acid; as that circulation of the fluid which takes place during the solution of other metals is wanting. When the acid contains nitrous gas the action is more rapid.‡ The nitrate of palladium, thus formed, is of a dark-red colour; by evaporation it yields a red matter, which is probably in the state of subnitrate.
- 4. Iodate of palladium. Iodate of potash when mixed with chloride of palladium, throws down a yellowish precipitate.§

<sup>\*</sup> Chenevix on Palladium, Phil. Trans. 1803.

<sup>+</sup> Berzelius.

Wollaston on the Discovery of Palladium. Phil. Trans. 1805.

Pleischl.

- 5. Arseniate of palladium. A light yellow matter.\*
- 6. Oxalate of palladium. Oxalate of ammonia throws down nitrate of palladium light yellow.+
- 7. Citrate of palladium. Citrate of potash gives with nitrate of palladium a light yellow precipitate.
- 8. Benzoate of palladium. Benzoate of ammonia throws down from chloride of palladium a white precipitate, which is soluble in a great quantity of water.§

#### SECTION XXXVII. - SALTS OF PEROXIDE OF RHODIUM.

The properties of the salts belonging to this genus are too imperfectly known to admit of a detailed description. Dr. Wollaston examined them, only so far as to show that their base is the oxide of a peculiar metal. A few additional facts have been stated by Berzelius. Only the salts of peroxide have been noticed, those of the protoxide are quite unknown.

These salts, so far as examined, have the following properties:

Characters.

- 1. The solution of them in water is red.
- 2. Prussiate of potash occasions no precipitate.
- 3. Neither is any precipitate produced by hydrosulphuret of potash.
- 4. Neither sal ammoniac nor the alkaline carbonates occasion any precipitate; but the pure alkalies throw down a yellow powder soluble in an excess of alkali.
- 1. Sulphate of rhodium. When hydrosulphuret of ammonia is mixed with soda-muriate of rhodium and heat applied a sulphuret of rhodium precipitates. When this sulphuret is treated with fuming nitric acid, it is converted into sulphate of rhodium, part of which dissolves in the acid, and another portion remains in the state of a black powder. When the whole nitric acid is driven off, the sulphate of rhodium remains behind. It deliquesces in the air and assumes a red colour. When dissolved in water and evaporated to dryness, it does not become black as at first, but a syrupy matter of an orange-colour which swells up in a greater heat and becomes spongy like calcinated alum. In that state it dissolves slowly in water, and after two or three days is entirely dissolved in that liquid if left in contact with it. Caustic potash precipitates from it a pale yellow substance, which appears to be a triple subsulphate.

<sup>\*</sup> Berzelius.

When exposed to a cherry-red heat sulphuric acid and oxygen gas are disengaged, leaving behind a black insoluble powder. This powder, according to Berzelius, is a sulphated protoxide of rhodium.\*

- 2. Nitrate of rhodium. The peroxide of rhodium dissolved in nitric acid forms a red solution which does not crystallize. The taste of this salt is exceedingly astringent.
- 3. Arseniate of rhodium. Arseniate of soda throws down a yellowish white precipitate from the solution of ammoniochloride of rhodium.
- 4. Acetate of rhodium. Acetic acid dissolves peroxide of rhodium. The solution is red and astringent.

The rest of the salts of rhodium are still unexamined.

#### SECTION XXXVIII.—SALTS OF PROTOXIDE OF IRIDIUM.

Iridium forms no fewer than four oxides, but the only salts Characters. upon which any experiments have hitherto been made, are those of the protoxide.

This genius of salts is still less known than the former. We are indebted to the French chemists, and to Mr. Tennent and to Berzelius for all the facts hitherto detailed.

- 1. The salts of iridium appear to be soluble in water, and to have a colour at first green, but which changes to red by concentrating the solution in an open vessel.
- 2. Neither prussiate of potash nor the infusion of nut-galls occasions any precipitate; but both render the solution colourless.
- 3. They appear to be partially precipitated by sal ammoniac; since Descotils has shown that the red colour which the muriate of platinum and ammonia sometimes assumes, is to be ascribed to the presence of iridium.

The solutions of the protoxide of iridium in acids have a dirty green colour. The solution in nitric acid when left to itself assumes a purple colour, but if it be evaporated to dryness by a gentle heat, and then dissolved, it assumes its original green colour.

#### SECTION XXXIX. -- SALTS OF OXIDES OF OSMIUM.

These salts are still almost entirely unknown.

Characters.

The salts of the protoxide have a dark-green colour like those of iridium, at least when in solution in water.

- \* Berzelius, Annals of Philosophy, iii. 256.
- + Berzelius, Kong. Vet. Acad. Handl. 1828, p. 69.

Class 1.

The salts of the sesquioxide are dark-brown, almost black.

The binoxide does not dissolve in acids. Its salts, there-

fore, are still quite unknown.

The quateroxide of osmium seems rather to possess the characters of an acid than a base.

#### SECTION XL.—SALTS OF OXIDE OF TELLURIUM.

The salts of tellurium have been very little examined, owing to the scarcity of tellurium, which has prevented most chemists from making it the subject of investigation. They may be distinguished by the following properties:

Characters.

- 1. They are transparent and colourless.
- 2. Alkalies, when dropped into their solution, occasion a white precipitate, which disappears again if the alkali be added in excess.
  - 3. Prussiate of potash occasions no precipitate.
- 4. Hydrosulphuret of potash occasions a brown or blackish precipitate.
- 5. The infusion of nut-galls occasions a flaky precipitate of a yellow colour.
- 6. Zinc, iron, and antimony, when plunged into these solutions, occasion the tellurium to separate in the state of a black powder, which resumes its metallic brilliancy when rubbed.\*
- 7. Sulphite of ammonia, when added to a solution of tellurium, throws down a black powder consisting of tellurium in the metallic state.
- 8. Hydrosulphuret of ammonia added in excess to a solution of tellurium, throws down a black precipitate, which is redissolved by digestion if the quantity of hydrosulphuret be sufficient.
- 1. Sulphate of tellurium. When one part of tellurium is confined with 100 parts of sulphuric acid in a close vessel, it dissolves and gives the acid a crimson colour. When water is dropped into the acid, the red colour disappears, and the metal is precipitated in black flakes. When heated, the colour equally disappears, and the metal precipitates in the state of a white powder. Diluted sulphuric acid, mixed with a little nitric acid, dissolves a considerable portion of tellurium, the solution is colourless, and no precipitate is produced in it by water.†
  - 2. Sulphite of tellurium does not exist, sulphurous acid having
    - \* Klaproth's Beitrage, iii. 1; and Crell's Annals, 1798, i. 98.

† Crell's Annals, 1798, i. 98.

the property of depriving oxide of tellurium of its oxygen, and sect. XLII. reducing it to the metallic state.

3. Nitrate of tellurium. Nitric acid dissolves tellurium with facility. The solution is colourless, and not rendered turbid by water. It yields, when concentrated, small, white, light, needle-form dendritical crystals.\*

When the neutral salt is heated pretty strongly, it is partly decomposed, and a white salt is obtained in the state of a white powder, which still reddens litmus paper.

- 4. Phosphate of tellurium. A white powder, insoluble in water.
  - 5. Arseniate of tellurium. A white insoluble powder.§
  - 6. Molybdate of tellurium. A white insoluble powder.
  - 7. Tungstate of tellurium. A white insoluble powder.
- 8. Chromate of tellurium. A yellow powder. Obtained by double affinity.
- 9. Bichromate of tellurium. A syrupy, not crystallizable mass.¶
- 10. Benzoate of tellurium. Benzoate of ammonia throws down from the salts of tellurium a white powder, nearly insoluble in water.\*\*

The rest of the tellurium salts are still unknown.

#### SECTION XLI.-SALTS OF WHITE OXIDE OF ARSENIC.

It is well known that white oxide of arsenic possesses the properties of an acid and not of a base. Hence no salts in which this substance acts the part of a base seem to exist. Sulphuric acid, and muriatic acid, when digested over the arsenious acid dissolve a portion, but the sulphuric acid lets it fall again on cooling, and if we attempt to dilute the muriatic acid solution with water, the greatest part of the arsenious acid precipitates.

## SECTION XLII. - SALTS OF PROTOXIDE OF ANTIMONY.

Of the three oxides of antimony only the first or lowest has the properties of an alkali, and those in a state of imperfection. The other two oxides possess acid properties, and accordingly have been distinguished by the name of antimonious and antimonic acids. Such of the salts of these acids as are known have been described in the preceding sections.

The solution of protoxide of antimony, which is best known,

\* Crell's Annals, 1798, i. 98. † Berzelius. ‡ Ibid. § Ibid. ¶ John. • \*\* Hisinger.

and which has been most examined, is the muriatic. It becomes milky when diluted with water, but if an excess of muriatic acid be added the precipitate is again redissolved.

Characters.

- 1. Potash or ammonia added to this solution throws down a white precipitate, which is not redissolved by adding an excess of the alkali.
- 2. The same effects are produced by carbonate of potash and carbonate of ammonia.
- 3. Phosphate of soda and oxalic acid also occasion a white precipitate.
- 4. Prussiate of potash occasions a white precipitate when dropped into these solutions. This precipitate is merely the oxide of the metal precipitated by the water of the prussiate. When applied sufficiently concentrated, or in crystals, no precipitation takes place. In this property antimony agrees with platinum.\*
- 5. Hydrosulphuret of ammonia occasions an orange-red precipitate, which redissolves in an excess of the precipitant.
- 6. When a plate of iron or zinc is plunged into antimonial solutions, a black powder precipitates in great abundance, and very speedily when there is an excess of acid, and the solution is not too much concentrated.
- 1. Sulphate of antimony. When antimony is heated in concentrated sulphuric acid, sulphurous acid is evolved, sulphur sublimes, and a white neutral salt is obtained, which is soluble in dilute sulphuric acid, but when water is poured on it a supersulphate of antimony dissolves, while a subsulphate is left in the state of a white powder.

When the neutral salt is heated it gives off sulphurous acid and oxygen, and, according to Bussy, some anhydrous sulphuric acid. The subsulphate formed by means of water is composed, according to Souberan, of

Sulphuric acid	17.99
Protoxide of antimony	82.01
	100.00+
This approaches	•
1 atom sulphuric acid	5
$2\frac{1}{2}$ atoms protoxide of antimony	<b>23.75</b>
	-
	28.75

<sup>\*</sup> Klaproth, Crell's Annals, 1798, i. 99.

<sup>†</sup> Jour. de Pharmacie, x. 532.

2. Sulphite of antimony. This salt may be obtained by digesting protoxide of antimony in sulphurous acid, or by passing a current of sulphurous acid gas through a solution of muriate of antimony. It is insoluble in water.\*

3. Nitrate of antimony. Concentrated nitric acid oxidizes antimony without the application of heat. The same effect is produced by dilute acid provided heat be applied. Water seems to be decomposed as well as nitric acid, and nitrate of ammonia formed. Very little of the protoxide of antimony is held in solution by the acid. The undissolved portion, however, may be combined with nitric acid, and forms a white powder, which, according to Bucholz, is composed of

	Muric acia	•	•	•	19.00
ŕ	Protoxide of a	ntimony	•	•	84.66
					100
This app	roaches pretty:	nearly to			
	l atom nitric a		•		6.75
	4 atoms protos	xide of an	timoı	ny	38
					44.75

- 4. Croconate of antimony. Croconate of potash when mixed with a solution of chloride of antimony throws down a lemonyellow precipitate, soluble in an excess of chloride of antimony.
- 5. Phosphate of antimony. Liquid phosphoric acid dissolves a little protoxide of antimony. The solution does not crystallize, but when evaporated leaves a blackish green mass, which in a high temperature may be fused into a transparent glass.
- 6. Phosphite of antimony. Phosphite of ammonia occasions no precipitate in tartar emetic, but when muriatic acid is added, a white precipitate falls, which, after being dried and heated, yields pure hydrogen.§
- 7. Arseniate of antimony. Arseniate of potash throws down a white precipitate from muriate of antimony.
- 8. Arsenite of antimony. This salt may be obtained by digesting arsenic acid upon metallic antimony. It precipitates when the liquid is diluted with water. We may form the salt by heating a mixture of arsenic and antimonic acid. In that case it constitutes a glassy, translucent matter.
  - 9. Chromate of antimony. Chromate of potash gives with
    - \* Berzelius. † L. Gmelin. ‡ Wenzel.
    - § Mitcherlich, Ann. de Chim. et de Phys. xxxv. 217.

<sup>|</sup> Berzelius. | Ibid.

muriate of antimony a brownish-yellow precipitate, which, in an excess of muriate of antimony, dissolves and becomes green, owing obviously to the decomposition of the chromic acid.

- 10. Molybdate of antimony. A yellow powder, soluble in boiling water.\*
- 11. Oxalate of antimony. Oxalic acid scarcely attacks antimony, but it dissolves a small portion of its oxide. The solution yields by evaporation small crystalline grains difficultly soluble in water. The same salt is precipitated by adding oxalic acid to the solution of antimony in acetic or sulphuric acid, but oxalic acid occasions no precipitate in butter of antimony.+
- 12. Acetate of antimony. Acetic acid has little or no action on antimony, but it dissolves a small portion of its oxide, as Morveau has shown, and the solution, according to Wenzel, vields small crystals. This salt is soluble in water, and was employed by Angelus Sala and some subsequent physicians as an emetic.§
- 13. Tartrate of antimony. Tartaric acid by the assistance of heat dissolves a little protoxide of antimony. When this solution is concentrated to the consistence of a syrup, and washed with alcohol, it dissolves readily in water and reddens The solution is not precipitated by water, but is thrown down by the sulphuric acid salts and by nitric acid.
- 14. Succinate of antimony. Succinic acid does not attack antimony, but it dissolves a portion of its protoxide, and forms a salt which has not been examined.
- 15. Benzoate of antimony. Benzoic acid readily dissolves the oxide of antimony, and the solution yields crystals, which remain dry when exposed to the air, and are decomposed by heat.\*\* This salt dissolves readily in water and alcohol.
- 16. Gallate of antimony. Sublimed gallic acid precipitates tartar emetic white.

#### SECTION XLIII. -- SALTS OF PROTOXIDE OF CHROMIUM.

The green oxide of chromium combines with the different acids and forms a genus of salts which has not hitherto been much investigated by chemists. They may be distinguished by the following characters:

- \* Berzelius.
- † Verwandtschaft, p. 158.
- || Soubeiran and Schnaubert.
- \*\* Trommsdorf, Ann. de Chim. xi. 317.
- + Bergman, i. 271.
- § Encyc. Method. Chim. i. 6.
- ¶ Wenzel.

- 1. The solutions of salts of chromium have usually a darkgreen colour, though some of them are blue and some of them characters.
  purple: The intensity of the colour is such that most of them are opaque even when dilute. When evaporated to dryness they do not crystallize, but leave an opaque matter, of so deep a green, that it appears to the eye black.
- 2. The taste of these solutions is a very strong and rather agreeable sweet, peculiarly pleasant when they are rendered slightly acidulous by an excess of acid.
- 3. Potash throws down a green precipitate, which is again dissolved by adding the alkali in excess.
- 4. Ammonia and its carbonate also throw down a green precipitate.
- 5. Prussiate of potash occasions no precipitate, but when the mixture is heated it becomes dark-brown and opaque, yet no precipitate falls.
- 6. The infusion of nut-galls throws down a green precipitate in flocks.
- 7. Sulphuretted hydrogen occasions no precipitate, provided the salt of chromium be free from all traces of chromic acid. Hydrosulphuret of ammonia throws down a precipitate in green flocks, probably in consequence of an excess of ammonia.
- 8. When benzoate of potash is dropped into a concentrated solution of muriate of chromium a green flocky precipitate falls, but no precipitate falls when the solution is dilute.
- 1. Sulphate of chromium. Hydrated protoxide of chromium dissolves easily when digested in dilute sulphuric acid, forming a solution having a dark-green colour, and a sweet and slightly acidulous taste. When evaporated to dryness a very dark-green tasteless matter remains. It does not redden litmus paper, and is easily reduced to powder. It is not altered by exposure to the air, and seems at first insoluble in water. But when digested with water on the sand-bath a solution is slowly effected, having the same colour, taste, and properties, as at first. Its constituents, by my analysis, are

13.375

'The whole acid cannot be driven off by the heat of a common wind furnace.\*

Class L

- 2. Sulphite of chromium. According to Vauquelin, sulphurous acid readily dissolves the hydrated protoxide of chromium.

  3. Nitrate of chromium. Nitric acid dissolves hydrated
- 3. Nitrate of abromium. Nitric acid dissolves hydrated protoxide of chromium with facility. The solution has a reddish-blue colour, and however long the digestion was prolonged, I never succeeded in saturating the acid. The solution is sweet and acidulous, and when evaporated to dryness, leaves a reddish-blue matter, readily soluble in water, and not very deliquescent. When this salt is heated, it melts, and copious fumes of deutoxide of azote are given off. When the heat is continued till these fumes cease to be disengaged, a portion of the green oxide has been converted into chromic acid. The matter dissolves in water, and constitutes a dark-brown liquid, which is a chromate of chromium. From an imperfect analysis of nitrate of chromium, I am disposed to consider it as a compound of

1 atom nitric aci	d	•	•	•	6.75
1 atom protoxide	e of ch	romit	ım	•	5
3 atoms water	•	•	•	•	3.375
					15.125*

4. Biphosphate of chromium. This salt is obtained by mixing together solutions of phosphate of soda and chloride of chromium. While immersed in the liquid from which it has been precipitated, it has a dirty white colour; but when washed and dried, it is a very fine deep green. It is quite tasteless,

and insoluble in water. Its constituents, by my analysis, are

T moobmorre	acia	•	•	•	•	
Protoxide o	f chron	nium		•	•	5.00
${f Water}$	•	•	•	•	•	6.63†
This approaches no	earest t	0				
2 atoms pho	sphori	c acid		•	•	9
l atom protoxide of chromium					•	5
6 atoms wa	ter	•	•	•	•	6.75
						20.75

I did not succeed in obtaining a neutral phosphate of chromium.

5. Arseniate of chromium. When arseniate of soda and muriate of chromium are mixed together, the mixture evaporated to dryness, and the residue digested in water till it refuses to take up any thing else, arseniate of chromium remains

Phosphoric acid

<sup>\*</sup> Phil. Trans. 1827, p. 205.

in the state of a fine green, tasteless, and insoluble powder. I seet. XLIII. found it a compound of
Arsenic acid 6.67
Protoxide of chromium
Protoxide of enformation
11.67*
This approaches
1 atom arsenic acid
1 atom protoxide of chromium . 5
12.25
6. Binarseniate of chromium. This salt was obtained by
digesting arsenic acid upon hydrated oxide of chromium till it
refused to take up any more. A dark-green solution was
formed, which was evaporated to dryness, and the residue
digested in water till nothing more was taken up. A dark-
green insoluble matter remained, which was tasteless. When
heated to redness it became rose-red; but on cooling assumed
a buff colour. It was found by analysis to be a compound of
Arsenic acid 15.8
Protoxide of chromium 5.0
Water 6.65
27·45†
This approaches pretty nearly to
2 atoms arsenic acid 14.5
1 atom protoxide of chromium . 5
6 atoms water 6.75
**************************************
26.25
7. Dicarbonate of chromium. When muriate of chromium
is precipitated by carbonate of soda, the precipitate, after
washing and drying in a low heat, is a light-blue coloured
matter, very light, tasteless, and insoluble in water. Its con-
stituents I found to be
1 atom carbonic acid 2.75
2 atoms protoxide of chromium . 10
A

4 atoms water

4.5

17.25‡

<sup>8.</sup> Triscarbonate of chromium. Meissner mentions a car-

<sup>\*</sup> Phil. Trans. 1827, p. 212. † Ibig.

<sup>‡</sup> Ibid. p. 208.

Class I.	bonate o	f chromium	obtained	by double	decomposition,	which
		composed		•	•	

Carbonic acid .		•	•	15.539
Protoxide of chrom	ium	•	•	<b>77.300</b>
Water	•	•	•	· 7·161
	•			100.000
This approaches nearest to				
l atom carbonic aci	d			2.75
3 atoms protoxide o	of chre	omium		15
1 atom water	•		•	1.125
				18.875

9. Pentacarbonate of chromium. I obtained this salt by employing bicarbonate of potash to precipitate the muriate of chromium. It is a light-blue, tasteless powder, and was a compound of

1	atom o	carbonic	acid	•	•	•	2.75
5	atoms	protoxid	le of c	hromi	um	•	<b>25</b>
21	atoms	water	•	•	•	•	23.725
							51:175

I could not succeed in my attempts to form a neutral carbonate of chromium.

10. Chromate of chromium. When chromic acid is digested on hydrated green oxide of chromium, a solution takes place, and the liquid assumes a dark-brown colour. When we dissolve as much of the oxide as possible, and evaporate the solution to dryness, a brown insoluble powder is obtained, to which the name of brown oxide of chromium was formerly given.

When we mix together solutions of chromate of potash and muriate of chromium, a brown powder of the same nature falls; but it is soluble in water, and I have reason to believe that the solution, if properly treated, would yield crystals of chromate of chromium.

- 11. Molybdate of chromium. When molybdate of potash is mixed with muriate of chromium, an apple-green precipitate falls.
- 12. Oxalate of chromium. Oxalic acid digested over hydrated green oxide of chromium, dissolves it with facility. The solution has a deep violet colour, and an excessively sweet taste.

When evaporated to dryness it deliquesces again. When sect. X III. heated, so as to expel the greatest portion of the water, we obtain 'a greenish-black matter, quite tasteless, and similar to charcoal in appearance. When this powder is digested in water it gradually dissolves, and the solution has the colour and taste of a solution of oxalate of chromium. The constituents of this salt are

1 atom oxalic acid	•	•	4.5
1 atom protoxide of chromium		•	5
3 atoms water	•	•	3.375
			10.975

- 13. Binoxalate of chromium. According to Moser, the preceding salt dissolves in oxalic acid, and yields, when evaporated, octahedral crystals of binoxalate of chromium.
- 14. Acetate of chromium. When strong acetic acid is digested in a flask over hydrated protoxide of chromium, several days elapse before any solution takes place, though the action be assisted by heat. But by degrees the liquid assumes a green colour, which gradually deepens. But the acid cannot be saturated in this way, the smell continuing, and the liquid retaining an acid taste, though it becomes also sweet. When evaporated, a dark green matter remains, no longer soluble in water, but soluble as before when digested in acetic acid.\*
- 15. Tartrate of chromium. Tartaric acid gradually dissolves hydrated oxide of chromium, and forms a dark blue coloured liquid having the usual sweet acidulous taste, which characterizes the salts of chromium. When the liquid is evaporated to dryness, a black, brittle, tasteless powder remains, which is tartrate of chromium. It is not easy to saturate the acid; but when this is accomplished the constituents are

			15.5
2 atoms water	• •	•	2.25
1 atom protoxide of chromium	•	•	5
1 atom tartaric acid	•	•	8.25

According to Moser, octahedral crystals may be obtained from a solution of protoxide of chromium in tartaric acid. These crystals probably consist of *bitartrate* of chromium.

- 16. Citrate of chromium. Hydrated protoxide of chromium dissolves in citric acid, and the solution, when evaporated, yields prismatic crystals, having a light green colour.
  - \* Phil. Trans. 1827, p. 214. 

    † Brandenburg.

- 17. Succinate of chromium. When the succinic acid is digested over hydrated protoxide of chromium, a green solution is formed, which, by spontaneous evaporation, yields octahedral crystals of a dark violet colour.\*
- 18. Oleate of chromium. When muriate of chromium and oleate of potash are boiled together, a double decomposition takes place, and oleate of chromium formed. It is a violet coloured matter. For some days it remains soft, but it gradually becomes quite hard when kept in a dry atmosphere.

#### SECTION XLIV. -- SALTS OF PROTOXIDE OF URANIUM.

Uranium is so scarce a metal that its salts have hitherto been very imperfectly examined. The protoxide has a green colour, and its solutions in acids are distinguished by a similar colour.

- 1. The taste of the salts of protoxide of uranium is astringent.
- 2. Caustic potash dropt into a solution of protoxide of uranium, throws it down green.
- 3. Prussiate of potash throws down a brownish-red precipitate, which does not assume the form of flakes, like prussiate of copper.
- 4. Gallic acid strikes a chocolate-brown colour, at least when the salt is neutral.
- 5. Sulphuretted hydrogen occasion's no precipitate, but hydrosulphuret of ammonia throws down a brownish-yellow powder.
  - 6. No precipitate is occasioned by zinc, iron, or tin.
- 1. Sulphate of uranium. Obtained by dissolving the protoxide in boiling sulphuric acid. A light green imperfectly crystallized saline mass. The solution is deep bottle-green, and by long exposure to the air it absorbs oxygen, and is converted into sulphated peroxide of uranium.‡
- 2. Nitrate of uranium does not seem to exist, as nitric acid has the property of changing protoxide of uranium into peroxide.
- 3. Carbonate of uranium. When sulphate of uranium is mixed with an excess of carbonate of ammonia, a light green precipitate falls.§

#### SECTION XLV. - SALTS OF PEROXIDE OF URANIUM.

This genus of salts has been much more examined than the preceding.

‡ Bucholz, Arfvedson. .

<sup>\*</sup> Moser.

<sup>+</sup> Chevreul, sur les corps gras, p. 96.

<sup>§</sup> Arfvedson.

- 1. The colour of the salts of peroxide of uranium is yellow, sect. XLV. and their taste astringent.
- 2. Most of the characters given to the preceding genus of salts belong also to this.
- 3. Carbonate of ammonia throws down a yellow precipitate, which is redissolved by an excess of carbonate. Solution lemon-yellow.
- 4. Carbonate of soda, a yellow precipitate redissolved by an excess of the precipitant.
- 5. Chromate of potash, a fine ochre-yellow precipitate of great intensity.
  - 6. Phosphate of soda, a yellowish-white precipitate.
- 1. Sulphated peroxide of uranium. Sulphuric acid, whether concentrated or diluted, has but little effect upon uranium, in the metallic state.\* By boiling the oxide obtained from nitrate of uranium by means of heat, with a sufficient quantity of diluted sulphuric acid, and setting the solution aside in a warm place, Mr. Bucholz obtained needle-form crystals of sulphate of uranium. As these crystals contained an excess of acid, though a portion of the oxide remained undissolved, Bucholz redissolved them in water, added a little nitric acid, and boiled them to dryness over a new portion of oxide of uranium. The mass was dissolved again in water, filtered, and set aside. After some months very small prismatic crystals separated; and by continuing the evaporation some crystals were obtained in the shape of tables.

The colour of these crystals is lemon-yellow. They dissolve in  $\frac{5}{8}$ ths of their weight of cold water, and in  $\frac{9}{20}$ ths of their weight of that liquid when boiling hot. The solution has the consistency of a syrup, and gradually yields regular crystals when subjected to spontaneous evaporation. Pure alcohol at the common temperature of the air dissolves  $\frac{1}{25}$ th part, and boiling alcohol  $\frac{1}{20}$ th part of its weight of them. When the solution was exposed to the sun, its colour, at first light yellow, became green, and the whole of the oxide gradually precipitated, carrying along with it a portion of sulphuric acid. At the same time the smell of ether became perceptible in the liquid.

When crystallized sulphated peroxide of uranium is exposed to a red heat, it loses 14 per cent. of its weight; but in a white heat it loses the whole of its acid and water. The residue, which weighs  $\frac{4.6}{10.0}$ ths of the original salt, is a grayish-black powder, consisting of protoxide of uranium.

<sup>\*</sup> Bucholz, Gehlen's Jour. N. 36,

This salt, according to the experiments of Bucholz, to whom we are indebted for the whole of the facts above enumerated, is composed of

18 acid 70 oxide 12 water

100\*

Now if the atomic weight of peroxide of uranium be 28, these numbers are equivalent to

1.44 atom sulphuric acid,

1 atom peroxide of uranium,

4.26 atoms water.

Hence it is probable that the true constitution of this salt is

1 atom sulphuric acid	•	•	7.5
1 atom peroxide of uranium	•	•	<b>2</b> 8
4 atoms water	•	•	4.5
			40

I made repeated analyses of this salt, prepared by digesting carbonated peroxide of uranium in dilute sulphuric acid, till it refused to take up any more. In one analysis I got precisely the theoretic quantities given above; but in general there was a small excess of acid. This leads to the suspicion that a bisulphated peroxide of uranium also exists.†

2. Sesquinitrated peroxide of uranium. This salt is best formed, as Klaproth showed, by dissolving the carbonated peroxide of uranium in nitric acid, and bringing the solution to crystallization. The best method of obtaining regular crystals is to expose the solution to a very moderate heat. saturated hot solution is cooled quickly, crystals likewise are obtained, but not so regular. The crystallization succeeds best when there is a slight excess of acid. † The colour of the crystals varies somewhat according to the method of crystallizing. When the solution is fully saturated with oxide, the crystals are of a lemon-yellow, and greenish at the edges; but when there is an excess of acid present, they have all a greenish colour. The crystals have the form of tables, often hexagonal; but by cautious management, they may be obtained in large four-sided rectangular flat prisms.§

They are extremely soluble in water; 93 parts of that liquid

<sup>\*</sup> Gehlen's Jour. iv. 134.

<sup>+</sup> First Principles, ii. 26.

<sup>‡</sup> Bucholz, Gehlen's Jour. iv. p. 145.

<sup>§</sup> Ibid. 146.

at the common temperature being capable of dissolving 200 Sect. XLV. parts of nitrated peroxide of uranium. Boiling water dissolves any quantity; the water of crystallization being sufficient at that temperature to keep the salt in solution. They are still more soluble in pure alcohol; one part of that liquid dissolving 31d parts of the nitrate. The solution has a yellow colour, and is of the consistence of a syrup. Boiling alcohol dissolves any quantity, but a portion of the salt precipitates again as the solution cools. By evaporation the solution yields regular crystals of nitrate and peroxide of uranium. If it be kept for a long time in the temperature of about 112°, the salt is partly decomposed, a yellow powder precipitating; a portion of which is peroxide of uranium, and a portion of the same oxide united probably to a vegetable acid. When four parts of this salt and one part of alcohol are distilled in a very moderate heat, the first portion which comes over has the smell of nitric ether; the second contains a portion of acetic acid.\*

Sulphuric ether dissolves about one-fourth of its weight of this salt; the solution is lemon-yellow; but when exposed to the sun's rays, it becomes in a few minutes green, and in some hours a watery portion subsides, of a green colour, containing The ether acquires the smell of nitric ether, and a uranium. quantity of protoxide of uranium precipitates.+

When nitrated peroxide of uranium is exposed to the air at the temperature of about 100°, it very soon falls into a white powder; but in cold and damp air it very soon deliquesces into a liquid.

When heated, it undergoes the watery fusion; the water which it contains is gradually dissipated, carrying along with it a portion of the acid. If the heat be increased, nitrous gas makes its escape, and at last a portion of oxygen gas is disengaged. By this process, not only the whole of the acid and water is dissipated, but the metal loses also a considerable portion of its oxygen.§

From the experiments of Bucholz, it follows that this salt is composed of

> 61 oxide 25 acid 14 water

100

<sup>\*</sup> Bucholz, Gehlen's Jour. iv. p. 151. § Ibid. p. 149. ‡ Ibid. p. 150.

<sup>†</sup> Ibid. p. 156. | Ibid. p. 148.

## Class I. This is equivalent to

1.69 atom nitric acid,

- 1 atom peroxide of uranium,
- 5 atoms water.

I analyzed the salt, and obtained for the constituents

1 atom nitric acid	•	•	10.125
1 atom peroxide of uranium	•	•	<b>2</b> 8
17 atoms water	•	•	19·125
			57.25*

The reason of the great excess of water was, that no steps were taken to dry the crystals, except leaving them for some time exposed to the air. I am disposed to consider the quantity of water assigned by Bucholz, as nearer the truth than mine.

- 3. Carbonated peroxide of uranium. This salt in a state of purity is unknown. When a salt of peroxide of uranium is precipitated by carbonate of potash or ammonia, not added in excess, the yellow precipitate contains the precipitating alkali as well as carbonic acid and peroxide of uranium.
- 4. Sesquiphosphated peroxide of uranium. When ammonia is added to a superphosphated peroxide of uranium, a yellowish white precipitate falls scarcely soluble in water, but readily soluble in carbonate of ammonia. According to the analysis of Laugier, the constituents of this salt are

Phosphoric a	cid		•	•	16.6
Peroxide of u	ıran	ium	•	•	61
Water	•	•		•	22

99.6+

This is equivalent to

1.69 atom phosphoric acid

1 atom peroxide of uranium

8.9 atoms water.

Hence the constitution of the salt is probably

$1\frac{1}{2}$	atom phosphor	ic acid	i	•	•	6.75
1	atom peroxide	of ura	anium	•	•	28
9	atoms water	•	•	• .		10.125
						44.875

<sup>\*</sup> First Principles, ii. p. 24.

<sup>†</sup> Ann. de Chim. et de Phys. xxiv. 239.

- 5. Superphosphated peroxide of uranium. This salt may be obtained by dissolving carbonated peroxide of uranium in an excess of phosphoric acid. It is a yellow, uncrystallizable, gelatinous substance, attracting moisture when exposed to the air.\*
- 6. Arseniated peroxide of uranium. A light yellow powder insoluble in water.
- 7. Borated peroxide of uranium. Obtained by precipitating a salt of peroxide of uranium with borax. A light yellow powder, very little soluble in water.+
- 8. Selenited peroxide of uranium. The neutral salt is a lemon-yellow powder, which, when heated, allows its acid with a portion of oxygen to escape, and leaves a green coloured oxide. The biselenite is formed by dissolving the preceding salt in selenic acid. When evaporated it leaves a pale yellow transparent varnish. When quite dry it is white, opaque, and crystalline.‡
- 9. Chromated peroxide of uranium. Chromate of potash throws down a fine orange precipitate from the sesquinitrated peroxide of uranium.
- 10. Bichromated peroxide of uranium. When carbonated peroxide of uranium is dissolved in an excess of chromic acid and the solution concentrated, it deposites small cubic crystals and dendrites. The salt melts at a low red heat, and is partially decomposed.§
- 11. Bimolybdated peroxide of uranium. Molybdate of ammonia throws down from sesquisulphated peroxide of uranium a light sulphur yellow powder, composed of

100 |

This is equivalent to

2.43 atoms molybdic acid

1 atom peroxide of uranium.

Hence there can be little doubt that its true constitution is

46

When this salt is heated it becomes blue. It is insoluble

\* Richter. † Ibid. ‡ Berzelius, Ann. de Chim. et de Phys. ix. 266. § John. | Brandes.

- in water, but dissolves in the stronger acids and in carbonate of ammonia.
  - 12. Tungstated peroxide of uranium. A light yellow powder, insoluble in water, but soluble in the stronger acids and in carbonate of ammonia.\*
  - 13. Oxalated peroxide of uranium. This salt may be obtained by dissolving the hydrated peroxide of uranium in an aqueous solution of oxalic acid, or by decomposing sesquinitrated peroxide by a concentrated solution of oxalic acid. A yellowish white powder in small crystalline grains. It is scarcely soluble in water. According to the analysis of Berzelius, it is a compound of

l atom oxalic acid .	•	•	4.5
1 atom peroxide of uranium	•	•	28
3 atoms water	•	•	3.375
			35.875

14. Teroxalated peroxide of uranium. I obtained this salt by digesting a dilute solution of oxalic acid in carbonated peroxide of uranium till the liquid refused to take up any more. This solution was very nearly composed of

3 atoms oxalic acid 1 atom peroxide of uraniu	· ım	.•	•	13·5 28
				41.5

But when evaporated it deposited crusts of the common oxalated peroxide. †

- 15. Acetated peroxide of uranium. Concentrated acetic acid dissolves peroxide of uranium by digestion, and yields beautiful yellow crystals in the form of long, slender, transparent, four-sided prisms terminated by four-sided pyramids. When heated gradually, the acid is decomposed and driven off, but the remaining oxide still retains the form of the crystals. ‡
- 16. Tartrated peroxide of uranium. Obtained by mixing perchloride of uranium with tartrate of potash. Small whitish yellow crystalline grains, very little soluble in water. Tartaric acid does not prevent peroxide of uranium from being thrown down by alkalies.§
- 17. Pyrotartrated peroxide of uranium. When pyrotartrate of potash is mixed with sesquinitrated peroxide of uranium a white crystalline precipitate gradually falls.
  - \* Berzelius. † First Principles, ii. 28.
  - ‡ Klaproth, Crell's Annals, i. 135. Eng. Trans. § H. Rose. | Ibid.

- 18. Citrated peroxide of uranium. A very light yellow salt, scarcely soluble in water.\*
- 19. Malated peroxide of uranium. A light yellow powder, very little soluble in water.
- 20. Succinated peroxide of uranium. Obtained by double decomposition. A light yellow matter, very little soluble in water.
- 21. Benzoated peroxide of uranium. Obtained in the same way as the preceding, which it resembles in its properties.
- 22. Gallated peroxide of uranium. Sublimed gallic acid gives a reddish brown colour to acetated peroxide of uranium, and by degrees a precipitate having the same colour falls.
  - 23. Camphorated peroxide of uranium. A yellow powder.
- 24. Sesquisuberated peroxide of uranium. Suberate of ammonia throws down from sesquisulphated peroxide of uranium a light yellow precipitate, which on drying becomes yellowish white; but resumes its original colour when boiled in water. It is tasteless, and composed, according to the analysis of Brandes, of

Suberic acid .	•	•	•	41.684
Peroxide of uranium		•	•	58:316
				100·000¶

# This comes very near

1 atom peroxide of uranium	•	28
		46.75

25. Pinated peroxide of uranium. Obtained by double decomposition. When boiled in oil of turpentine it is converted into a dark brown liquid.\*\*

## SECTION XLVI.-SALTS OF PROTOXIDE QF MOLYBDENUM.

This genus of salts has been very little examined. The most of them have a green, brown, and black colour, similar to a solution of sesquioxide of manganese in cold muriatic acid, without the evolution of chlorine. The taste is simply astringent, without any thing metallic. They are not so apt to absorb oxygen as the salts of deutoxide of molybdenum, and

<sup>\*</sup> Richter. † Ibid. 

† Ibid. 

§ Ibid.

<sup>||</sup> Brandes, Schweigger's Jour. xxxviii. 300. | Ibid. xxxiii. 99.

<sup>\*\*</sup> Unverdorben, Poggendorf's Annalen, xi. \$36.

may therefore be concentrated without so much risk of alteration. Sometimes (especially when they have an excess of acid) they assume a purple colour, precisely like the salts of sesquioxide of manganese in the same circumstances.

- 1. Sulphate of molybdenum. It may be obtained by dissolving the hydrated protoxide of molybdenum in sulphuric acid. The solution is almost black. When dry protoxide is triturated with concentrated sulphuric acid, we form a black tough mass, which is a neutral salt, if the quantity of oxide be sufficient. When water is poured upon this matter, it undergoes decomposition, a supersulphate being dissolved, while a subsulphate remains insoluble. The solution when concentrated becomes black and tough, but not crystalline. When the supersulphate is heated, sulphurous acid is evolved, and the salt is converted into sulphated deutoxide of molybdenum.\*
- 2. Nitrate of molybdenum. This salt is obtained by dissolving hydrated protoxide of molybdenum in dilute nitric acid. The solution has at first a black colour, which speedily passes into purple.

When an excess of hydrated oxide is employed, we obtain a subsalt. This salt cannot be preserved, the oxide gradually absorbs oxygen from the acid, and is at last converted into molybdic acid.†

- 3. Carbonate of molybdenum. Berzelius could not succeed in forming this salt.
- 4. Phosphate of molybdenum. Obtained by mixing solutions of chloride of molybdenum and phosphate of soda. The precipitate is at first redissolved, but soon becomes permanent. It has a dark gray colour, and is soluble in an excess of chloride of molybdenum.

When the hydrated protoxide is dissolved in phosphoric acid, we obtain a dark purple supersalt, having a syrupy consistence, deliquescing in the air, and dissolving in ammonia.

- 5. Arseniate of molybdenum. This salt is quite similar to the preceding.
- 6. Borate of molybdenum. A dark gray precipitate, which becomes black when dried.
- 7. Chromate of molybdenum does not seem capable of being formed. The protoxide of molybdenum deprives the acid of oxygen, and converts it to green oxide.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 163.

- 8. Oxalate of molybdenum,
- 9. Acetate of molybdenum,
- 10. Tartrate of molybdenum,

11. Succinate of molybdenum, precipitates, which become black when dried.\*

These four salts may be ob- Sect. XLVII. tained by double decomposition. They are dark gray

## SECTION XLVII. - SALTS OF DEUTOXIDE OF MOLYBDENUM.

The salts of deutoxide of molybdenum, while they retain water of crystallization, are red; but when deprived of their water, they become almost black. Their solutions have an astringent taste, and communicate at the same time an impression of acidity, and leave a feeling of something metallic in the mouth.

When infusion of nut-galls is added to a solution of these Characters. salts, the colour becomes bright yellow, with a shade of brown, and a small quantity of grayish-brown matter precipitates.

Prussiate of potash throws down a dark brown precipitate, which is not redissolved by an excess of the precipitant.

A rod of zinc causes them to assume a black colour, and protoxide of molybdenum mixed with zinc gradually precipitates.

The insoluble salts of deutoxide of molybdenum, when put into an alkaline solution, become black, because the oxide is changed into molybdic acid, and is taken up, provided there be a sufficient quantity of alkali.

- 1. Sulphated deutoxide of molybdenum. This salt may be formed by dissolving hydrated deutoxide in sulphuric acid, or by decomposing the muriate by sulphuric acid. The solution is red, but when evaporated to dryness, it becomes black. When evaporated in a high temperature, it becomes light blue, a change to which the salts of deutoxide of molybdenum are very liable.+
- 2. Nitrated deutoxide of molybdenum. This salt may be obtained either by dissolving hydrated deutoxide in nitric acid, or by digesting an excess of molybdenum in dilute nitric acid. It may be much concentrated, but it cannot be obtained in a solid state without becoming blue. Indeed, when rendered quite solid, it is quite colourless, the deutoxide being converted into molybdic acid.
  - 3. Phosphated deutoxide of molybdenum. When muriated

t Ibid. † Ibid. p. 153.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 168.

deutoxide of molybdenum is mixed with phosphate of ammonia, this salt precipitates in the form of light red flocks. The liquid retains a yellowish colour, a proof that the salt is not quite insoluble.

When hydrated deutoxide is digested in phosphoric acid as long as any thing will dissolve, a superphosphate is obtained, which by spontaneous evaporation dries into a red, tough, translucent substance, not in the least crystalline. Ammonia dissolves this salt, assuming a red colour; but in about an hour the liquid becomes muddy, and most of the salt falls down. When the ammoniacal solution is exposed to the air, it soon loses its red colour.\*

- 4. Arseniated deutoxide of molybdenum is obtained when the muriated deutoxide is mixed with an arseniate. It has a great tendency to become blue, even when left to spontaneous evaporation. It dissolves in caustic ammonia, communicating a deep red colour. No precipitate falls when the liquid is abandoned to itself, but it gradually loses its colour.
- 5. Borated deutoxide of molybdenum is insoluble in water. It falls of the colour of rust of iron when muriate of deutoxide is mixed with borate of ammonia. When hydrated deutoxide is dissolved in boiling boracic acid, a yellow liquid is obtained, which on cooling deposites the neutral borate.‡
- 6. Silicated deutoxide of molybdenum is obtained when fluosilicated deutoxide is decomposed by means of ammonia. When it is left for some days in the ammoniacal solution, the deutoxide is changed into molybdic acid and dissolved, while the silica remains behind.
- 7. Chromated deutoxide of molybdenum is soluble in water, with a light yellow colour. The solution, when left to spontaneous evaporation, gives yellow coloured needles, which when fully dried become white.

Superchromated deutoxide dissolves in water with a brown colour. By evaporation it is converted into a vitreous-looking brown mass, which is still soluble in water.

When either of the preceding solutions is mixed with ammonia, a subchromate precipitates in grayish yellow flocks, insoluble in water.

8. Quatermolybdated deutoxide of molybdenum. This is the molybdous acid of Bucholz—a blue matter, soluble in water. From the analysis of Berzelius, it appears to be a compound of

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 157.

<sup>†</sup> Ibid. † Ibid. § Ibid. | Ibid.

4 atoms molybdic acid .		36	Sect. XLVII.
1 atom deutoxide of molybdenum		8	
		44	
The result of the experiments was			
Molybdic acid		83	
Deutoxide of molybdenum	•	17	
·		100*	

This amounts to about

4.34 atoms molybdic acid,

- 1 atom deutoxide of molybdenum.
- 9. Tungstated deutoxide of molybdenum. When a mixture of muriated deutoxide and tungstate of ammonia is made, the solution assumes a beautiful purple colour, but so deep, that it is opaque, unless in very thin layers. The colour can be seen in all its beauty by diluting the solution sufficiently. When the concentrated liquid is mixed with sal ammoniac, the purple coloured matter falls down. This matter may be collected on the filter, and washed first with a solution of sal ammoniac, and then with alcohol of the sp. gravity 0.86, in which it is not soluble. It is now a purple coloured mass, which is not altered by exposure to the air, and which is completely soluble in water. The solution gradually loses its colour, in consequence of the acidifications of the molybdenum. This salt is decomposed by caustic soda, deutoxide of molybdenum being thrown down.†
- 10. Oxalated deutoxide of molybdenum is soluble in water. The crystals obtained by spontaneous evaporation are bluish, almost black, but they dissolve with a red colour in water. Ammonia throws down from the solution a dark tile-red subsalt, which is not redissolved by an excess of the alkali.‡
- 11. Acetated deutoxide of molybdenum is precipitated when muriated deutoxide is mixed with acetate of potash. The salt has the colour of deutoxide of molybdenum. Hydrated deutoxide dissolves in boiling acetic acid with a yellow colour. The solution gelatinizes on cooling. When left to itself it dries into a dark brown powder.§
- 12. Tartrated deutoxide of molybdenum dries into a pale red gummy mass, which has a great tendency to become green or

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 174.

blue. It is not precipitated by the alkalies, but forms with them a dark red solution, which speedily becomes colourless when exposed to the air.\*

13. Succinated deutoxide of molybdenum behaves precisely like the acetated salt.+

#### SECTION XLVIII. - SALTS OF MOLYBDIC ACID.

It has been for some time known that molybdic acid has the property of combining with acids, and of acting the part of a base; but the only person who has hitherto examined these compounds is Berzelius.

Characters.

Molybdic acid does not combine with water; but when molybdenum or its oxides are acidified by nitric acid, this acid dissolves molybdic acid, and when diluted with water has a yellow colour; but it speedily becomes muddy, and deposites molybdic acid in the form of a white powder. When this precipitate is washed and dried, it is a white matter, which, when ignited, gives out about one per cent. of water. The ignited mass is soft to the touch, and may be spread upon the skin. In this state it dissolves easily in acids and forms the genus of salts which it is the object of this section to describe.

- 1. Sulphated molybdic acid. Molybdic acid dissolves with a yellow colour in sulphuric acid. When the solution is evaporated to dryness a lemon-yellow matter is obtained, a part of which only is again soluble in water. When it is exposed to the air it deliquesces, and the crystals previously formed disappear. When a saturated solution of this salt is boiled with molybdic acid in excess, we obtain a milky liquid, which gelatinizes on cooling, and deposites light yellow flocks, which may be considered as a subsulphate of molybdic acid. It is partly soluble in water, but not in spirits, which, however, give it a green colour.
- 2. Nitrate of molybdic acid. This salt does not exist; for molybdic acid does not form any combination with nitric acid, which can be obtained in a solid state.
- 3. Phosphate of molybdic acid. When molybdic acid while still moist, is put into phosphoric acid, it becomes immediately lemon-yellow, and then is dissolved by the assistance of heat. The filtered solution is colourless, and when evaporated leaves

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Hand. 1825, p. 159. † Ibid. p. 160.

<sup>‡</sup> Kong. Vet. Acad. Handl. 1825, p. 169.

<sup>§</sup> Berzelius, ibid. p. 170.

a transparent tough mass, which does not crystallize, and has Sect. XLVIII. a strong astringent taste. It dissolves easily both in water and spirits: The solution in spirits has a green colour; when evaporated it becomes blue, and leaves a brown opaque matter, which dissolves in water with a blue colour.

When molybdic acid in excess is digested with phosphoric acid, a lemon-yellow subsalt is formed.\*

- 4. Arseniate of molybdic acid. This salt formed in the same way as the preceding, gives a transparent colourless solution, and a lemon-yellow subsalt. When evaporated to the consistence of a syrup, it crystallizes. Spirits decompose the crystals, and separate white flocks, which, however, are afterwards dissolved. When the solution is evaporated, it becomes blue, and does not again crystallize.†
- 5. Borate of molybdic acid. Boracic acid dissolves molybdic acid when assisted by a boiling heat. When there is an excess of molybdic acid, the matter after evaporation becomes transparent and adhesive like turpentine. The solution becomes milky on cooling. The filtered liquid is colourless, and gives, after evaporation, a crystallized colourless salt. Spirits decompose the crystals, separate a yellow powder, and dissolve boracic acid with a very small quantity of molybdic acid.‡
- 6. Chromate of molybdic acid. Chromic acid dissolves molybdic acid when assisted by a boiling heat. The solution is yellow. When an excess of molybdic acid is employed the whole is converted to a yellow translucent jelly. The filtered solution being evaporated leaves a yellowish-brown varnish. Water decomposes it into a brownish matter easily soluble, and a light yellow powder, which, however, may be again dissolved by the addition of more water. §
- 7. Oxalate of molybdic acid. This salt is easily obtained by digesting the two acids together. The solution is colourless, and it does not acquire colour even when an excess of molybdic acid is employed. By evaporation a colourless jelly is obtained, which, by farther evaporation, assumes a crystalline form. The salt dissolves completely, and with a yellow colour, in spirits.
- 8. Acetate of molybdic acid is obtained when molybdic acid is boiled in acetic acid. When the molybdic acid is in excess the solution is opaque and milky. The liquid by concentration yields a colourless jelly, which, by farther concentration,

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 171.

- becomes yellow, and assumes the form of a coarse yellow powder, which is very slightly soluble in water, tinging the liquid yellow.\*
  - 9. Tartrate of molybdic acid is a colourless, not crystallizable salt. It always becomes blue during the evaporation. The salt is completely soluble in spirits.+
  - 10. Succinate of molybdic acid is made by the same process as the others. The solution is colourless; but gives yellow crystals when concentrated. Alcohol separates from it a yellow powder and dissolves most of the succinic acid.‡

#### SECTION XLIX.—SALTS OF TUNGSTIC ACID.

This genus of salts is almost completely unknown. Though the protoxide of tungsten, in all probability, will be found hereafter capable of uniting with acids and forming salts, yet not one of these salts has been hitherto examined. It would be useless, therefore, to attempt to lay down characters by which these unknown bodies might be recognised. The following constitute the only salts belonging to this genus hitherto attended to.

- 1. Sulphate of tungstic acid. When concentrated nitric acid is mixed with the aqueous solution of tersulphuret of tungsten, or when sulphuric acid is added to a solution of tungstate of ammonia, a white heavy precipitate falls, which is a compound of sulphuric acid, tungstic acid, and water. It is soluble in water, but again thrown down by nitric or sulphuric acid. When heated to redness it gives out sulphuric acid and water, and pure tungstic acid remains. §
- 2. Nitrate of tungstic acid. When nitric acid is added to a solution of tungstate of ammonia a lemon-yellow precipitate falls, which is a compound of nitric and tungstic acids. It dissolves in water with a yellow colour, and is again precipitated by the addition of nitric acid.

#### SECTION L .- SALTS OF COLUMBIC ACID.

The oxides of columbium possess the characters of acids; but the peroxide or columbic acid would appear, from the observations of Ekeberg, to be capable also of uniting to some acids, and of forming a genus of salts still almost unknown. The only facts respecting them, with which I am acquainted, are the following:

\* Berzelius, Kong. Vet. Acad. Handl. 1825, p. 172. † Ibid. p. 173. † Ibid. p. 173. † Ibid. p. 174.

- 1. Sulphate of columbic acid. This salt may be obtained by Sect. LL dissolving columbic acid in sulphuric acid. Water precipitates from the solution the columbic acid still united with a portion of sulphuric acid and analogous to a subsalt.\*
- 2. Phosphate of columbic acid. Columbic acid and phosphoric acid may be melted together into a colourless glass.+
- 3. Borate of columbic acid. Boracic acid and columbic acid may be fused together into a transparent colourless glass.‡
- 4. Tungstate of columbic acid. It appears from the observations of Gahn, Berzelius, and Eggertz, that this salt may be formed, but no description of it has been given.

#### SECTION LI.—SALTS OF TITANIC ACID.

Though titanium forms two combinations with oxygen, yet it is only the peroxide or titanic acid that has yet been combined with acids, and of these we only know a very few and these imperfectly.

- 1. The characteristic property of solutions of titanium in Characters. acids is the bulky, dark, reddish brown precipitate, which falls on the addition of infusion of nut-galls, similar in appearance to coagulated blood.
- 2. Titanic acid is precipitated from its solutions by ammonia. The precipitate is very bulky and similar to alumina in appearance, but contracts much in size when dried.
- 3. It is thrown down from its solution in acids by boiling. But the precipitate cannot be washed. When we collect it on a filter the liquid passes colourless as long as it is acid, but when it becomes pure water it assumes a milky appearance, and the whole titanic acid passes along with it through the When the solution contains zirconia the whole titanic acid cannot be separated by boiling.
- 4. Titanic acid is not precipitated by sulphuretted hydrogen gas, nor by hydrosulphuret of ammonia added in excess.
- 5. When a rod of tin is plunged into a solution of titanium, the liquid around it gradually assumes a fine red colour. rod of zinc, on the other hand, occasions a deep blue colour.§
- 1. Supersulphate of titanic acid. It may be formed by mixing together 1 part of sulphuric acid, 1/2 part of water, with titanic acid in fine powder and recently ignited, and digesting till the water is dissipated, then apply a heat sufficient to drive

<sup>\*</sup> Berzelius. † Ekeberg. ‡ Ibid.

<sup>§</sup> Klaproth's Beitrage, i. 233.

off the excess of sulphuric acid (it must not be so high as ignition) and dissolve the residue in a little water. We obtain a colourless liquid, from which, by dilution with more water and the application of heat, a subsulphate of titanic acid may be precipitated.\*

2. Ennea-sulphate of titanic acid. This salt may be obtained by precipitating a muriatic acid solution of titanic acid by the addition of sulphuric acid. It is a white matter, which reddens litmus paper, and by ignition is converted into pure titanic acid. According to the analysis of Mr. H. Rose, the constituents of this salt are

			1		2
Sulphuric acid		•	7.78		7.56
Titanic acid	•	•	76.83		76.50
${f Water}$	•	•	15.39		15.94
			100.00		100.00
This is equivalent very n	early	y to			
1 atom sulphuric		•	•	•	5
9 atoms titanic ac			•		47.25
9 atoms water		•	•	•	10.125
			4		62:375

- 3. Nitrate of titanic acid. Nitric acid dissolves hydrated titanic acid, but the nature of the solution has not been determined. The rhombic crystals observed by Klaproth were not crystals of nitrate of titanium, but were derived from the alkali which his titanic acid contained.
- 4. Phosphate of titanic acid. This compound may be obtained by adding phosphoric acid to a solution of titanic acid in muriatic acid. It precipitates in bulky white flocks, soluble both in an excess of phosphoric acid and of muriate of titanic acid. When dried it is a gum-like matter having considerable lustre.
- 5. Arseniate of titanic acid. When arsenic acid is dropped into a solution of titanic acid in an acid, white flocks are thrown down, similar in appearance to alumina, and which when dried becomes a glittering glassy-like substance. It is soluble in an excess of arsenic acid, as well as of the titanic acid solution.
- 6. Hex-oxalate of titanic acid. When an acid solution of titanic acid is heated with oxalic acid a cheesy-looking precipitate falls. When dried, it has the property of reddening

moist litmus paper. This salt is soluble both in an excess of Sect. LII. oxalic acid and of the titanic solution.\*

According to the analysis of H. Rose, the constituents of this salt are

Oxalic acid	•	•	•	10.40
Titanic acid	•	•	•	74.16
$\mathbf{Water}$	•	•	•	15.44
		•		100.00
This approaches very nea	rly to			
l atom oxalic ac		٠.	•	4.5
6 atoms titanic	acid	•	•	31.5
6 atoms water		•	•	6.75
				42.75

- 7. Acetate of titanic acid. A gelatinous incrystallizable matter.
- 8. Tartrate of titanic acid. Obtained by precipitating muriate of titanic acid by tartaric acid. It is similar in its appearance to the hexoxalate of titanium, but when heated to redness in a covered crucible it is converted into a black metallic powder. When tartaric acid is added to an acid solution of titanic acid in such quantity as not to produce a precipitate, neither ammonia nor its carbonate are capable of throwing down any thing from the liquid.
- 9. Gallate of titanic acid. Sublimed gallic acid strikes a yellow colour with muriate of titanium. By degrees a brownish precipitate falls.

#### SECTION LII. -- OF COMPOUND OXYGEN ACID SALTS.

In the preceding sections an account has been given of the different simple oxygen acid salts so far as their properties have been investigated. But there are several of these simple salts that have the property of combining with each other, and of forming a new class of salts, to which, of course, the name compound salts may be given. Thus sulphate of potash and sulphate of ammonia unite together, atom to atom, and form a new compound salt which has been called ammonia-sulphate of potash. Such salts are very numerous, amounting at present to nearly 200, and doubtless the number will very much increase, as the attention of chemists is turned to such investiga-

<sup>\*</sup> Laugier and H. Rose.

<sup>+</sup> H. Rose, Poggendorf's Annaler, iii. 165.

tions. Doubtless when such combinations take place one of the salts acts the part of an acid and the other of a base, though it would not be easy in the present state of our knowledge to determine which is the acid and which the alkali. Most of the compound salts at present known consist of the union of two salts having the same acid each, though there are a few in which the acids differ as well as the bases.

In describing the compound salts I shall, in the first place, give an account of those in which one acid exists united to two bases, and then of the few at present known in which both the acids and bases are different. As the number is so great as to require subdivision, I shall arrange them according to the acid existing in each, and make the base, hypothetically considered, as constituting the alkali of the salt which constitutes the acid of the compound, the foundation of a farther subdivision.

## I. Compound salts of sulphuric acid.

These amount nearly to 50, constituting about one-fourth of all the compound salts at present known. They may be subdivided into 7 sets, according to the nature of the base of the hypothetical acid salt. This base, for the sake of distinctness, is always placed before the name of the acid in giving an appellation to the salt.

# 1. Ammonia-sulphates.

1. Ammonia-sulphate of potash. This salt was first described by Link, in 1796.\* It is easily formed by dissolving sulphate of potash and sulphate of ammonia in water in atomic proportions and evaporating the solution. It crystallizes in beautiful transparent prisms with square bases. The taste is bitter, the specific gravity 2.64. 100 parts of water dissolve 13.68 parts of this salt at the temperature of 61°. Its constituents are

2. Ammonia-sulphate of soda. This salt was likewise first described in 1796 by Link.‡ It may be formed by dissolving sulphate of soda and sulphate of ammonia in atomic proportions, and crystallizing the solution. The crystals are transparent

<sup>\*</sup> Crell's Annalen, 1796, i. 29. † First Principles, ii. 417.

<sup>‡</sup> Crell's Annalen, 1796, i. 30.

oblique prisms, with rhomboidal bases. Its taste is pungent Sect. LII. and bitter, it does not effloresce in the air, and contains less water than sulphate of soda. Its constituents are

1 atom sulphate of so	da	•	•	9
1 atom sulphate of ar	nmonia	•	•	7.125
6 atoms water	•	•	•	6.75
				99.875

3. Ammonia-sulphate of lithia. This salt was first described by Arfvedson. It crystallizes in tables, is easily soluble in water, and when heated leaves sulphate of lithia.

4. Ammonia-sulphate of magnesia. This salt may be formed by dissolving its two constituents in water in the atomic proportions and concentrating the solution, it crystallizes in large transparent crystals, which are oblique rhombic prisms, of the figure given in the margin. The following are the measurements as determined by Mr. Brooke.\*

P on M or M'	•	•	104° 45′
P on $e$ or $e'$	•	•	154 40
$\mathbf{P}$ on $g$	•		135 40
P on $c$		•	115 30
M on M'		•	109 30
$\mathbf{M}$ on $k'$	•	•	125 15

The crystals are not altered by exposure to the air. The salt has a bitter taste, and a specific gravity of 1.721. It dissolves readily in water. Its constituents, by my analysis, are

1 atom sulphate	of mag	gnesia	•	•	7.5
1 atom sulphate	of ami	monia	•	•	7.125
7 atoms water	•	•		•	<b>7·875</b>

22.5+

M

According to Mitcherlich, it contains 8 atoms of water.

5. Ammonia-sulphate of alumina or ammoniacal alum. Alum is a compound of three atoms sulphate of alumina with one atom of sulphate of potash, sulphate of soda, or sulphate of ammonia, and a certain portion of water. The common alum of this country contains sulphate of potash, but in France sulphate of ammonia is frequently substituted, constituting ammoniacal alum.

<sup>\*</sup> Annals of Philosophy (2d series), vii. 117.

<sup>+</sup> First Principles, ii. 419.

It is a transparent salt, which crystallizes in regular octahedrons. Its taste is acid and astringent, and it reddens vegetable blues. At the temperature of 60°, 100 parts of water dissolve 9.37 parts of this alum, but it is much more soluble in boiling water. When heated it swells, loses its water of crystallization, and is converted into a white mass usually called burnt alum. A strong red heat drives off the whole sulphuric acid and sulphate of ammonia, and leaves pure alumina. The constituents of this salt, by my analysis, are

1 ator	1 atom sulphate of ammonia			•	•	7.125
	ns sulphate				•	21.75
	ns water	•		•	•	28.125
						£7.0

The same salt has been analyzed on the continent, and found to contain only 24 atoms water.

6. Ammonia-trisulphate of alumina. Riffault informs us that when a boiling hot solution of the preceding salt is precipitated by the slow addition of ammonia, a white powder falls, which is a compound of

l atom sulp	phate o	of an	nmoni	a .	•	7.125
3 atoms tri	sulpha	te o	f alum	ina	•	35.250
9 atoms wa	ter	•	•	•	•	10.125
						52.5*

7. Ammonia-sulphate of iron. This salt is obtained by mixing solutions of sulphate of iron and sulphate of ammonia in the atomic proportions. The colour is a light green, and the shape of the crystals is, according to Mitcherlich, the same as that of ammonia-sulphate of magnesia. Its constituents, according to the analysis of Mitcherlich, are

			25.625
			-
8 atoms water	•	•	9.0
I atom sulphate of iron	•	•	<b>9·5</b>
l atom sulphate of ammonia	•	•	7.125

8. Ammonia-sulphated peroxide of iron. This salt has been lately described by M. Maus. It may be formed by adding ammonia cautiously to a solution of sulphated peroxide of iron, and leaving the liquid to spontaneous evaporation. The crystals are regular six-sided prisms. The colour is yellow, and

<sup>\*</sup> Ann. de Chim. et de Phys. xvi. 359.

it dissolves in 2.4 times its weight of cold water. Its constituents, according to the analysis of Maus, are

		•			100.00*
Water	•	•	•	•	16.75
Peroxide of iron	•	•	•	•	23.75
Ammonia	•	•	•	•	10.30
Sulphuric acid	•	•	•	•	49.20

This is obviously equivalent to

1 atom sulphate of ammonia .	•	7.125
1 atom sulphated peroxide of iron		10
3 atoms water .	•	3.375
		20.5

9. Ammonia-sequisulphated peroxide of iron. This salt was first prepared by Mr. Cooper of London, but it was Dr. Forchhammer who first pointed out its composition, and subjected it to analysis.† It is easily prepared by mixing solutions of sesquisulphated peroxide of iron and sulphate of ammonia in the proportions of two integrant particles of the former to one of the latter, and after concentrating the mixture somewhat, setting it aside. The new salt crystallizes in regular octahedrons. It is white, and has much of the taste and appearance of alum. It dissolves in about three times its weight of water at the temperature of 60°. Its constituents, by my analysis, are

2 atoms sesquisulphated peroxide	of iron	•	25
1 atom sulphate of ammonia	•	•	7.125
25 atoms water	•	•	28.125
			60.25

10. Ammonia-sulphate of manganese. This salt is obtained when solutions of sulphate of manganese and sulphate of ammonia are mixed in atomic proportions. The crystals have a light rose-red colour and the same form, according to Mitcherlich, as that of ammonia-sulphate of magnesia. They dissolve easily in water, and, according to John, deliquesce in a moist atmosphere. The specific gravity is 1.93. The constituents of this salt, according to my analysis, are

<sup>\*</sup> Poggendorf's Annalen, xi. 79.

<sup>†</sup> Annals of Philosophy (second series), v. 409.

Class I.	l atom sulphate of ammonia l atom sulphate of manganese	•	•	7·125 9·5
	7 atoms water	•		7.875

Mitcherlich makes the water 8 atoms.

11. Ammonia-disulphated sesquioxide of manganese. This salt, which was formed and described by Mitcherlich, has a dark red colour, and crystallizes in regular octahedrons like alum, which it resembles in many particulars. It crystallizes only in a very acid solution. When the crystals are dissolved in water, they undergo decomposition, the manganese being deposited. The composition of the salt, according to Mitcherlich, is

24.5

1 atom sulphate of ammonia	7.125
2 atoms sulphated sesquioxide of manganese	20.000
24 atoms water	27.000
	54.125

12. Ammonia-sulphate of nickel. It may be formed by mixing solutions of sulphate of ammonia and sulphate of nickel in the atomic proportions. The crystals, according to Mitcherlich, have the same shape as those of ammonia-sulphate of magnesia. They have a beautiful green colour, and a specific gravity of 1.801. Their constituents, according to my analysis, are

1 atom sulphate of ammonia	•	•	$7 \cdot 125$
1 atom sulphate of nickel	•	•	9.250
7 atoms water	•	•	7.875
			•
			24.25

Mitcherlich states the water as amounting to 8 atoms.

13. Ammonia-sulphate of cobalt. Red coloured crystals having the form of ammonio-sulphate of magnesia. Their constituents, according to the analysis of Mitcherlich, are

1 atom sulphate of ammonia	•	•,	7.125
1 atom sulphate of cobalt	•	•	9.25
8 atoms water	•	•	9.00
			25.375

14. Ammonia-sulphate of zinc. This salt is obtained by dissolving the two constituents in water in the atomic proportion, and concentrating the solution. It crystallizes in fine white

rhomboids, which have the characteristic taste of the zinc salts, sect. LIL and dissolves readily in water. Its constituents, by my analysis, are

I atom sulphate of	ammoi	nia	•	$7 \cdot 125$
1 atom sulphate of		•	•	10.25
7 atoms water	•	•	•	<b>7</b> ·8 <b>7</b> 5
			•	25.25

15. Ammonia-sulphate of copper. This salt is obtained by mixing the two constituents in the atomic proportions, and concentrating the solution. The crystals are oblique, flat, rhombic prisms, of a fine light-green colour. The salt reddens vegetable blues. Its constituents, according to my analysis, are

1 atom sulphate	of ammonia	•	7.125
1 atom sulphate	of copper		10
6 atoms water	• •		6.75

23.875

- 16. Ammonia-sulphate of mercury. This salt is difficultly soluble in water. It has not been examined by modern chemists.
- 17. Ammonia-sulphate of silver. This salt was formed by Mitcherlich by adding ammonia to a solution of sulphate of silver, and concentrating the solution. It crystallizes easily, and is very soluble in water. Its constituents, according to the analysis of Mitcherlich, are

1	atom	sulphate	of	ammonia	•	7.125
1	atom	sulphate	of	silver	•	19.75
						•
						26.875*

18. Ammonia-sulphate of platinum. This salt was formed by Mr. E. Davy, by neutralizing an aqueous solution of sulphate of platinum with ammonia, and boiling for a few minutes. The substance in question precipitates, and may be washed and dried.

It has a light brown colour, and is in powder or loosely aggregated lumps. It is tasteless, insoluble in water, and not altered by exposure to the air. It dissolves in muriatic acid,

<sup>\*</sup> Ann. de Chim. et de Phys. Axxv. 429.

and in sulphuric acid when assisted by heat. When nitric acid is boiled upon it, the substance is decomposed, and a black matter remains. It is insoluble in acetic acid, and very slightly soluble in phosphoric acid. It is decomposed by being boiled in a solution of the fixed alkalies. When heated, it is decomposed with a kind of imperfect detonation. Mr. E. Davy did not analyze it with precision, but infers, from an experiment, that its constituents are

Oxide of platinum Sulphate of ammonia	and	water	70 30
			100

- 19. Ammonia-sulphate of peroxide of uranium. This salt is obtained by mixing together solutions of sulphate of ammonia and sulphated peroxide of uranium in the atomic proportions, and concentrating the solution. It is a yellow salt, easily soluble in water, and reduced by a red heat to the state of protoxide of uranium.
- 20. Ammonia-sulphate of iron and zinc. This salt was obtained by Tassaert in his processes for obtaining cadmium from the metals which always accompany it. The alloy containing cadmium was dissolved in sulphuric acid, and a portion of ammonia was added to the solution. As long as there was a considerable excess of acid, nothing was precipitated by the zinc but cadmium; but when the acid was nearly saturated, small transparent crystals were deposited on the zinc. They are hard, and pretty soluble in water. The shape is the same as that of the variety of alum called by Haiiy primitive segminiforme. These crystals were analyzed by Tassaert, and found composed of

1 atom ammonia-	sulphate	e of i	ron	16.625
1 atom sulphate of	of zinc		•	10.25
$6\frac{1}{2}$ atoms water	•	•	•	<b>7·3125</b>
				34.1875*

### 2. Potash-sulphates.

1. Potash-sulphate of magnesia. This salt was first described by Link. He formed it by saturating supersulphate of potash with magnesia. Berthollet formed the same salt by mixing together equal solutions of sulphate of potash and

<sup>\*</sup> Ann. de Chim. et de Phys. xxiv. 100.

muriate of magnesia, and evaporating the mixture. The sect. LII. shape of the crystal is similar to that of ammonia-sulphate of magnesia. The taste is weak, but sensibly bitter. Its specific gravity is 2.112. It is not altered by exposure to the air. Its constituents, by my analysis, are

1 atom sulphate of potash 1 atom sulphate of magnesia. 7.5 7 atoms water 7.875

26.375

2. Potash-sulphate of alumina, or common alum. στυπτηρια of the Greeks, and the alumen of the Romans, was a native substance which appears to have been nearly related to green vitriol, or sulphate of iron; and which consequently was very different from what we at present denominate alum. From the researches of Professor Beckman, it appears that we owe the discovery of alum to the Asiatics; but at what period, or by what means, the discovery was made, is altogether unknown. It continued to be imported from the east till the 15th century, when a number of alum works were established in Italy. In the 16th century it was manufactured in Germany and Spain; and during Queen Elizabeth's reign an alum work was established in England by Thomas Chalomer. The alum of commerce is usually obtained from native mixtures of pyrites and clay, or sulphuric acid and clay.

Bergman has published a very complete dissertation on the

process usually followed.\* The earth from which it is procured is usually called alum slate, because it is slaty. colour is blackish, because it contains some bitumen. In most cases it is necessary to burn it before it can be employed; this is done by means of a slow smothered fire. Sometimes long exposure to the weather is sufficient to produce an efflorescence of alum on the surface. It is then lixiviated, and the water concentrated by evaporation, and mixed with putrid urine, or muriate of potash; crystals of alum and of sulphate of iron usually form together.

The composition of alum has been but lately understood with accuracy. It has been long known, indeed, that one of its ingredients is sulphuric acid; and the experiments of Pott and Margraff proved incontestibly that alumina is another in-

<sup>\*</sup> Opusc. i. 279.

<sup>+</sup> Some chemists have thought proper to call the sulphuric acid, obtained by distilling alum, spirit of alum.

gredient. But sulphuric acid and alumina are incapable of forming alum. Manufacturers knew that the addition of a quantity of potash or of ammonia, or of some substance containing these alkalies, is almost always necessary; and it was proved, that in every case in which such additions are unnecessary, the earth from which the alum is obtained contains already a quantity of potash. Various conjectures were made about the part which potash acts in this case; but Vauquelin \* and Chaptal † appear to have been the first chemists that ascertained by decisive experiments that alum is a douple salt, composed of sulphuric acid, alumina, and potash or ammonia, united together.

Alum crystallizes in regular octahedrons, consisting of two four-sided pyramids applied base to base. The sides are equilateral triangles. The form of its integrant particles, according to Hauy, is the regular tetrahedron. Its taste is sweetish and very astringent. It always reddens vegetable blues. specific gravity is 1.7109.‡ At the temperature of 60°, 100 parts of water dissolve 14.79 of this salt. It is soluble in  $\frac{3}{4}$ ths of its weight of boiling water. When exposed to the air it effloresces slightly. When exposed to a gentle heat it undergoes the watery fusion. A strong heat causes it to swell and foam, and to lose about 44 per cent. of its weight, consisting chiefly of water of crystallization. What remains is called calcined or burnt alum, and is sometimes used as a corrosive. By a violent heat, the greater part of the acid may be driven off. In that case, as was first observed by Milner, a portion of the acid is decomposed into sulphurous acid and oxygen gas. The constituents of this salt, by my analysis, are

1 atom sulphate of potash				11
3 atoms sulphate	•	21.75		
25 atoms water	•	•	•	28.125
				60.875

3. Potash-trisulphate of alumina. This salt formerly called alum saturated with its earth, may be obtained by adding potash to a boiling solution of alum, and washing the precipitate

<sup>\*</sup> Ann. de Chim. xxii. 258. † Ibid. 280.

<sup>†</sup> Hassenfratz, Ann. de Chim. xxviii. 12. Wallerius found it 1.719 (Chemistry, p. 266); and Dr. Watson, 1.757 (Essays, v. 67); Fahrenheit, 1.738. (Phil. Trans. liii. 114.)

<sup>§</sup> Bergman, i. 287.

till the water ceases to act on muriate of barytes. The conscitution stituents of the white tasteless powder thus obtained, are, according to the analysis of Riffault,

56.375\*

- 4. Potash-sulphate of yttria. Obtained by mixing solutions of the two constituents in the atomic proportions. It forms crystalline grains, not so soluble in water as sulphate of yttria, but more soluble than sulphate of cerium.
- 5. Potash-sulphate of cerium. This salt precipitates when an excess of sulphate of potash is put into a solution of cerium. It is a white powder, which melts when heated. It is very little soluble in water, and quite insoluble in water saturated with sulphate of potash. Slightly soluble in dilute sulphuric acid.‡ Its constituents, as determined by the analysis of Dr. Steel in my laboratory, are

1 atom sulphate of potash
1 atom sulphate of cerium
11.5
22.5

It is anhydrous.

6. Potash-sesquisulphate of peroxide of cerium. Obtained by mixing solutions of the two constituents in the atomic proportion. It is a lemon-yellow powder, difficultly soluble in water.§ It becomes white when washed or heated. Its constituents, as determined by the analysis of Dr. Steel in my laboratory, are

7. Potash-sulphate of zirconia. When an excess of sulphate of potash is added to a neutral salt of zirconia, a crystallized deposite takes place. This precipitate would appear, from the experiments of Berzelius, to be a compound of 1 atom of sulphuric acid and 6 atoms of zirconia, with a small quantity of potash, the exact amount of which has not been determined. It is very little soluble in water, and is precipitated again by

<sup>\*</sup> Ann. de Chim. et de Phys. xvi. 355. † Gahn and Berzelius. † Ibid.

sulphate of potash. When only slightly washed, it dissolves readily in water; but after having been thoroughly washed, or boiled in water, it becomes insoluble, or almost so, in acids, requiring for solution a great quantity of concentrated acid.\*

8. Potash-sulphate of iron. This salt was first formed by Link.+ It is easily formed by mixing solutions of sulphate of potash and sulphate of iron in the atomic proportions, and concentrating the solution. The colour is very light green, and the shape of the crystals, according to Mitcherlich, the same as that of ammonia-sulphate of magnesia. The taste is similar to that of sulphate of iron; but it is less soluble in water, and the solution, when heated, is apt to deposite flocks of peroxide of iron. Its constituents, by my analysis, are

1	atom sulphate	of po	tash	•	11
1	atom sulphate	of iro	n	•	9.5
5	atoms water	•	•	•	5.625
					26.125

According to Mitcherlich, it contains 6 atoms water.

9. Potash-sulphated peroxide of iron. When solutions of sulphate of potash and sulphated peroxide of iron are mixed and concentrated, there is usually a deposite of a greenish brown matter at the bottom of the vessel. This deposite is formed of crystals so much entangled together, and so small, that their form could not be made out. When dried in the open air, its colour was greenish yellow, and it was composed of grains seemingly cubical, having their solid angles rounded off, so as to approach the spherical form. The taste is astringent, sweetish, and acid. The salt reddens vegetable blues, and undergoes no alteration from exposure to the air. It dissolves in water with a yellow colour, and the solution is not quite transparent. Its constituents, by my analysis, are

1 atom sulphate	of po	tash	•	•	•	11
1 atom sulphated	l pero	oxide (	of iro	n	•	10
2 atoms water	•	•	•	•	•	2.25
						•

23.25

The same salt is described and analyzed by Maus. He obtained 3 atoms water. The rest of his analysis agrees with mine.‡

- 10. Potash-sesquisulphated peroxide of iron. This salt may
  - \* Berzelius. + Crell's Annalen, 1796, i. 30.

<sup>†</sup> Poggendorf's Anralen, xii. 78.

be obtained by mixing together solutions of sulphate of potash Sect. LU. be obtained by mixing together solutions of sulphate of potash and sulphated peroxide of iron in the requisite proportions, and crystallizing over sulphuric acid in the vacuum of an airpump. The crystals are transparent and colourless, and have the regular octahedral form of alum. The taste is similar to that of alum but harsher. When dissolved in water the liquid assumes a brownish red colour, and the salt cannot be again obtained in crystals. Hence water seems to decompose the salt. Its constituents, by my analysis, are

1 atom sulphate of potash		•	11
2 atoms sesquisulphated peroxide of iron		•	<b>25</b>
25 atoms water	•		28.125
			64.125

11. Potash-sulphate of manganese. This salt is obtained by mixing solutions of sulphate of potash and sulphate of manganese in the atomic proportions, and concentrating the solution. The crystals have the shape of those of ammonia-sulphate of magnesia. They have a fine flesh-red colour, and are not altered by exposure to the air. They are composed, by my analysis, of

I atom sulphate of potash .	•	•	11
1 atom sulphate of manganese	•	•	9.5
5 atoms water	•	•	5.625
			26.125

12. Potash-sesquisulphated sesquioxide of manganese. This salt is obtained when solutions of the two constituents are mixed and evaporated to the consistency of a syrup. Crystals are obtained, having the regular octahedral form of alum, a dark violet colour, and a taste having some resemblance to that of alum. When these crystals are dissolved in water they undergo decomposition. The constituents of this salt, according to the application of Mitcheslich and ing to the analysis of Mitcherlich, are

1	atom s	sulphate	of pota	sh	•	•	•	•	11
<b>2</b>	atoms	sesquisu	lphate	d sesq	uioxi	de of	mang	anese	<b>25</b>
<b>24</b>	$\mathbf{atoms}$	water	•	•	•	•	•	•	<b>27</b>
									00

13. Potash-sulphate of nickel. This salt was first described by Proust.\* It is easily formed by mixing sulphates of potash and zinc in the atomic proportion and concentrating the solu-

<sup>\*</sup> Jour. de Phys. xlvii. 169.

tion. It crystallizes in rhombic prisms, having a fine emerald green colour, and not altered by exposure to the atmosphere. Its specific gravity is 2.264. Its taste is sweet with an impression of bitterness. It is sparingly soluble in water. When heated it loses, according to Proust, about 24 per cent. of water. Its constituents, by my analysis, are

1 atom sulphate of potash	•	•	11
1 atom sulphate of nickel	•	•	9.25
6 atoms water	•	•	6·7 <b>5</b>
			97

Mr. H. Stokes found that when chromate of potash and sulphate of nickel are mixed in atomic proportions the residual liquid, after the deposition of the chromate of nickel, gives, when concentrated, fine crystals of potash-sulphate of nickel nearly pure.\*

14. Potash-sulphate of cobalt. This salt may be obtained by mixing its two constituents in the atomic proportions and concentrating the liquid. The crystals are oblique rhombic prisms, similar in shape to ammonia-sulphate of magnesia. The colour is red, and the salt, according to Proust, is less soluble in water than sulphate of cobalt. Its constituents, according to the analysis of Mitcherlich, are

1 atom sulphate of potash	•	•	411°
1 atom sulphate of cobalt	•	•	9.25
6 atoms water	•	•	6· <b>75</b>
			27

15. Potash-sulphate of zinc. This salt may be formed in the same way as the preceding. Its colour is white, and the crystals have the same shape as those of ammonia-sulphate of magnesia. Its taste is similar to that of sulphate of zinc. is not altered by exposure to the air, and it requires 5 times its weight of water to dissolve it. It was found by Mr. Stokes in the mother ley (after the deposition of bichromate of zinc) of sulphate of zinc and chromate of potash.+ The constituents of this salt, by my analysis, are

1 atom sulphate of potash	•	•	11
1 atom sulphate of zinc	•	•	10.25
7 atoms water	•	•	7.875
			29.125
* Phil. Mag. (2d series) ii. 428.			† Ibid.

<sup>\*</sup> Phil. Mag. (2d series) ii. 428.

- 16. Potash-sulphate of cadmium. This salt may be formed Sect. LII. by mixing together the two constituents in the atomic proportions, and concentrating the solution. The crystals, according to Mitcherlich, have the same form as those of ammonia-sulphate of magnesia.
- 17. Potash-sulphate of copper. This salt may be formed by mixing the two constituents in the atomic proportions, and concentrating the solution. It was first described by Vogel of Bayreuth. The crystals, according to Mitcherlich, have the same form as those of ammonia-sulphate of magnesia. The crystals have a bluish-green colour, and a specific gravity of 2.116. When held between the eye and the light two diagonals may be observed crossing the crystal, and of rather a lighter colour than the rest of the crystal. This salt is soluble in water, and may be obtained again in crystals unaltered. It suffers no change by exposure to the air. According to the analysis of Vogel of Bayreuth, to whom we are indebted for our knowledge of this salt, its constituents are

Sulphuric acid	•	•	•	36·0 <b>75</b>
Potash	•	•	•	21.425
Peroxide of copper	•	•	•	18.000
Water	•	•	•	24.500

100.000.\*

This analysis was confirmed in my laboratory. It is equivalent to

```
1 atom sulphate of potash
                                       11
1 atom sulphate of copper
                                       10
6 atoms water
                                        6.75
                                       27.75
```

Mr. Stokes formed this salt by mixing together chromate of potash and sulphate of copper in the atomic proportions.+

18. Potash-disulphate of copper. This salt was first accurately examined by M. Brunner. When solutions of sulphates of potash and of copper, in the atomic proportions, are mixed together and heated to the temperature of 140° or 150°, or still better if boiled, the liquid becomes muddy, and a light green, imperfectly crystallized powder falls, which is insoluble in water. The deposite, if the liquid be left over it, gradually concretes into a crust. The analysis of this salt, by Brunner, gave

<sup>\*</sup> Schweigger's Jour. vii. 40. † Phil. Mag. (2d. series) ii. 429.

3.97 atoms sulphuric acid
1.01 atoms potash
3.925 atoms oxide of copper
3.97 atoms water.\*

Numbers which show evidently that the true constitution of the salt is

4 atoms sulphuric acid,1 atom potash,4 atoms oxide of copper,

4 atoms water.

The salt therefore is a compound of

1 atom bisulphate of potash	•	•	16
2 atoms disulphate of copper	•	•	30
4 atoms water	•	•	4.5
			50.5

- 19. Potash-sulphate of platinum. This salt was formed by Vauquelin, by mixing together solutions of sulphate of potash and sulphate of platinum,† the liquid becomes colourless, and a dark bottle-green matter precipitates. When washed and dried it becomes black and shining, and when exposed to a red heat sulphurous and sulphuric acid are driven off, while a mixture of platinum and sulphate of potash remains.
- 20. Potash-subsulphated peroxide of platinum: When an aqueous solution of sulphate of platinum is neutralized by potash, and boiled for a few minutes, a dark brown substance falls and the liquid remains colourless. This precipitate constitutes the salt in question.

It is a dark brown or black substance, in grains not unlike those of gunpowder. It has a considerable lustre like that of blende. Its feel is harsh. It is tasteless, insoluble in water, not altered by exposure to the air, and not affected by boiling nitric acid. It is readily soluble in boiling muriatic acid; but nitro-muriatic acid has but little action on it. It is insoluble in boiling sulphuric, phosphoric, and acetic acids. Ammonia does not act on it. When boiled in a solution of potash no apparent effect is produced: but if the solution be boiled to dryness, and heated, two distinct compounds appear to be formed. The one yellow, and the other olive. It is insoluble in alcohol

Poggendorf's Annalen, xv. 476.

<sup>†</sup> Prepared by heating dichloride of platinum in sulphuric acid, till the liquid ceases to precipitate nitrate of silver, and then evaporating to dryness.

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and ether. In a red heat it is decomposed; oxygen, platinum, and sulphate of potash being produced. The constituents of this substance, according to the analysis of Mr. E. Davy, are as follows:

•	•	10.84
•	•	10.84
•		100:00
	•	

This must be admitted to be a very extraordinary compound, and seems hardly entitled to the name of a salt.

- 21. Potash-sulphate of uranium. A grayish-green powder, scarcely soluble in water.\*
- 22. Potash-sulphated peroxide of uranium. This salt may be formed by mixing together solutions of sulphate of potash and of peroxide of uranium in the atomic proportion, and evaporating the mixture. The salt is deposited in small globules, consisting of needles diverging from a centre. It has a fine lemon-yellow colour, an astringent taste, with an impression of bitterness, and it dissolves readily in water. Its constituents, by my analysis, are

1 atom sulphate of potash .	•	11
1 atom sesquisulphate of peroxide of uranium	n.	35.5
4 atoms water	•	4.5
		51

## 3. Soda-sulphates.

- 1. Soda-sulphate of lithia. A very difficultly soluble salt. It contains the third of its weight of sulphate of lithia.+
- 2. Soda-sulphate of lime. This salt is found imbedded in rock-salt, about ten leagues south of Madrid, at Vela Rubia, and in the blue salt of Ischel in Upper Austria. It is called glauberite by mineralogists. The crystals are oblique rhombic prisms, and the constituents, according to the analysis of Brogniart, are

1 atom sulphate of soda	•	•	9
1 atom sulphate of lime	•	•	8.5

17.

3. Soda-sulphate of magnesia. This salt was first described

<sup>\*</sup> Berzelius.

by Link, in 1796.\* It was afterwards analyzed by Dr. Murray,† who did not appear to have been aware of the previous experiments of the German chemist. Link obtained it by saturating bisulphate of soda with magnesia, and crystallizing the solution. Dr. Murray observed it formed in the boilers of the manufacturers of sulphate of magnesia from the bittern of sea salt. The impure sulphate of magnesia first obtained is redissolved in water and crystallized. A fresh quantity is added to the residual liquor, and by the necessary evaporation and cooling, a fresh crop of crystals is obtained. This is repeated a third and fourth time. It is in these last crystallizations that the triple salt is produced, forming frequently in considerable quantities, and precipitating even in the boilers. It is at first irregular and semitransparent; but by solution in water, and a second crystallization, it may be obtained in pretty regular transparent rhombs, truncated on their angles and edges. These crystals are not altered by exposure to the air. They have a bitter taste. At 60° they dissolve in about thrice their weight of water. When heated they do not melt, but decrepitate. Its constituent, according to the analysis of Murray, are

1 atom sulphate of soda	•	•	9
1 atom sulphate of magnesia	•		7.5
6 atoms water	•	•	6.75
			09.05

4. Soda-sulphate of alumina, or soda alum. This salt was perhaps first formed about the year 1805 by Charles Macintosh, Esq., of Cross Basket. Mr. W. Wilson of Hurlet, near Glasgow, furnished me with beautiful specimens of it about the year 1823. It was noticed in 1810 by Mr Winter, in his account of the Whitby alum processes.‡ It may be formed by adding sulphate of soda to a solution of alumina, but on account of its great solubility in water, it is not easily obtained in crystals. The crystals are regular octahedrons, like those of common alum, its taste also is the same. It undergoes no alteration by exposure to the air if pure; but when impure it effloresces on the surface. 100 parts of water at the temperature of 60° dissolve 327.6 parts of it. Its constituents, according to my analysis, are

<sup>\*</sup> Crell's Annals, 1796, i. 30. † Nicholson's Jour. xxv. 254.

<sup>96,</sup> i. 30. + Edin. Trans. viii. p. 233.

l atom sulphate of soda			9	Sect. LII.
3 atoms sulphate of alumina		•	21.75	
25 atoms water	•	•	28.125	
			58·8 <b>75</b>	

In its other properties it resembles common alum.

5. Native soda-alum. This salt occurs in the province of St. Juan near the city of Mendoza, in South America. It is found in nodules rather less than the size of a hen's egg, seemingly imbedded in slate. It is white and composed of fibres, adhering longitudinally, and having a certain breadth, but very thin. Harder than gypsum, which it resembles somewhat in appearance. The specific gravity is 1.88. It tastes like alum, and one part of water at 60° dissolves 3.773 parts of it. When heated it behaves like common alum. Its constituents, as determined in my laboratory, are

l atom sulphate of soda	•	•	9
3 atoms sulphate of alumina	•	•	21.75
20 atoms water	•	•	22.5
			<del></del>
			53.25

Hence it differs from artificial soda-alum, in containing 5 atoms less water. I have specimens of this salt from other parts of South America.

6. Soda-subsulphated peroxide of platinum. This salt may be obtained by a similar process as the potash subsulphated peroxide which it resembles in its properties. Its constituents, according to the analysis of Mr. E. Davy, are as follows:

Protoxide of platinum	•	•	84.16
Sulphate of soda	•	•	7.11
Water	•	•	8.73
			100.00

## 4. Baryto-Sulphatės.

1. Baryto-subsulphated peroxide of platinum. When a solution of muriate of barytes is poured into aqueous sulphate of platinum, a brown precipitate falls, which is the substance in question. It is tasteless, insoluble in water, and in boiling muriatic and nitric acids. Warm nitro-muriatic acid dissolves it, and so does sulphuric acid at a boiling temperature. It is not decomposed by the alkalies. When heated to redness, it gives out only water; no gas whatever is evolved. Mr. E.

Davy, to whom we are indebted for these facts, did not analyze this compound.

#### 5. Alumina-Sulphates.

1. Alumina-sulphate of platinum. When muriate of alumina is poured into sulphate of platinum a gelatinous brown precipitate falls, which is the salt in question. It is a black shining powder, insoluble in water, and not altered by exposure to the air. It is insoluble in the cold mineral acids, and only slightly acted on by these acids at a boiling temperature. When heated to redness, it gives out merely water, and becomes lighter coloured. It contains at least 27 per cent. of water; but Mr. E. Davy, to whom we are indebted for the preceding facts, did not analyze it.

#### 6. Ferro-sulphates.

1. Ferro-sulphate of alumina. This salt occurs rather abundantly in the waste coal pits round Glasgow, being crystallized in the shale in white, silky, very fine needles, like asbestus, easily fusible, and completely soluble in water. A specimen from an unknown locality, analyzed by Berthier, was composed of

Sulphuric acid	•	•	•	$34 \cdot 4$
Protoxide of iron	•	•		12.0
Alumina		•	•	8.8
Magnesia	, •		•	0.8
Water	•	•	•	44.0
				100*

### This is equivalent to

1 atom sulphate of iron	•	9.5
$1\frac{1}{2}$ atom sulphate of aluminate	a .	10.875
15 atoms water .	•	16.875
		37:25

But the constitution of the feather alum, so abundant at the Hurlet and at Campsie, both in the neighbourhood of Glasgow, is quite different. According to the analysis of Mr. R. Phillips, its constituents are as follows:

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Sulphuric acid	•	•	•	30.9	
Protoxide of iron	•	•	•	20.7	
Alumina	•	•		<b>5·2</b>	
Water	•	•	•	43.2	
				100.0*	

This approaches (though there is a slight deficiency of acid) to

<b>2</b>	atoms sulphate of iron	•	19
1	atom sulphate of alumin	a .	7.25
$16\frac{2}{3}$	atoms water .	•	18.675
			44.925

- 2. Perferro-sulphate of alumina. This salt contains peroxide of iron. It crystallizes in regular octahedrons, and is therefore analogous to alum.+
- 3. Ferro-sulphate of nickel. This salt may be obtained by mixing together the solutions of nitrate of nickel and sulphate of iron, and evaporating the mixture, or by dissolving at once the oxides of nickel and iron in sulphuric acid. The salt crystallizes in tables, its colour is green, and it effloresces when exposed to the atmosphere.‡
- 4. Ferro-sulphate of zinc. This salt is easily obtained by mixing together solutions of sulphate of iron and sulphate of zinc in atomic proportion, and concentrating the mixture. It crystallizes in rhombic prisms, having nearly the shape of sulphate of iron. Colour pale green. Specific gravity 1.980. Its taste and solubility are those of sulphate of zinc. It is not altered by exposure to the air. Its constituents, by a analysis, are

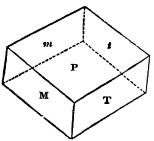
1 atom sulphate of iron		9.5
1 atom sulphate of zine		 10.25
14 atoms water	•	15.75
		35.5

5. Ferro-sulphate of copper. This salt may be obtained by mixing solutions of sulphate of iron and sulphate of copper,

II.

<sup>\*</sup> Annals of Philosophy (2d series), v. 446.

<sup>+</sup> Mitcherlich. ‡ Link, Crell's Annals, 1796, i. 32.



and concentrating the solution. The crystals formed have a fine blue colour with a shade of green. They seem, from the observations of Beudant, to have the shape of sulphate of iron. I always obtained them in flat rhombohedrons, as represented on the margin. Its angles, measured by the common goniometer, were

M on T	•	•	1009
M on m	• "	•	80
P on M	•	•	100
P on T	_	_	80

Its taste is cupreous, and its specific gravity 1.98. 100 parts of water at 60° dissolve 75.91 parts of it. The constituents of this salt, by my analysis, are

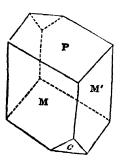
1 atom sulphate of iro	m .	•	$9 \cdot 5$
4 atoms sulphate of co	pper	•	40.0
34 atoms water	•	•	38.25
			97.75

According to Beudant, the salt is capable of existing with various proportions of sulphate of iron. The constituents of the whole salt which I procured, were as I have stated above.

6. Ferro-sulphate of nickel-and-copper. This salt is said by Link to be formed when the solution of nickel in nitric acid is mixed with sulphate of copper. It crystallizes, according to him, in blue coloured prisms, terminated by four-sided pyramids, and when exposed to the air falls to powder, but his experiments would require to be verified by repetition.\*

## 7. Nickel-sulphates.

1. Nickel-sulphate of copper. This salt was accidentally



met with by Dr. Brewster among some specimens of sulphate of nickel which he had received from Mr. Brandes, and from Mr. Badams of Birmingham. The nature of the salt was determined by Dr. Fyfe. The salt has a fine green colour, and is crystallized in oblique rhombic prisms as figured in the margin. The measurement of the angles by Mr. Brooke† are as follows:

<sup>\*</sup> Link, Crell's Annals, 1796, i. 31.

<sup>†</sup> Annals of Philosophy (2d series), vii. 117.

P on M or M'	•	•	100	)° 15′	Sect. LII.
$\mathbf{P}$ on $\boldsymbol{c}$	•	•	117	7 30	
M on M'	•	•	8	3 30	
According to the analysis of	Dr.	Fyfe,	its co	nstituents are	
Sulphuric acid		•	•	25.5	
Protoxide of nicke	el 🥙	•	•	39.5	
Oxide of copper		•	•	<b>5·3</b>	
Water .	•	. •	•	29.7	
				100.0*	
This is equivalent to					
·1 atom disulphate	of c	opper	•	15	
9 atoms disulphate	e of a	nickel	•	121.5	
53 atoms water		•		59.625	
				and the second s	

196.125

2. Nickel-sulphate of zinc. Zinc dissolves with effervescence in sulphate of nickel containing an excess of acid. The solution when concentrated yields light green crystals having the shape of the oblique crystals of sulphate of nickel. The taste is sharp, astringent, and metallic. It readily effloresces in the air into a white powder. It is soluble in 3 or 4 times its weight of cold water?

## 8. Cobalt-sulphates.

1. Cobalt-sulphate of zinc. This salt, first pointed out by Link, may be obtained by digesting zaffre in sulphate of zinc. Large four-sided prisms are obtained by evaporation, which effloresce when exposed to the air.‡

#### II. Compound salts of sulphurous acid.

This division is at present far from numerous, because chemists have not turned much of their attention to the salts of sulphurous acid.

#### 1. Ammonia-sulphites.

1. Ammonia-sulphite of magnesia. This salt has only been mentioned by Fourcroy. It may be formed by mixing together the solution of sulphite of ammonia and sulphite of magnesia, or by pouring ammonia into the sulphite of magnesia.

<sup>\*</sup> Edin. Phil. Jour. v. 208. † Tupputi. † Crell's Annals, 1796, i. 32.

Class 1.

- Its crystals are transparent, but the figure has not been determined. It is less soluble in water than either of its component parts. When exposed to the air, it is gradually converted into sulphate.
  - 2. Ammonia-sulphite of silver. Obtained by dissolving sulphite of silver in an aqueous solution of sulphite of ammonia. When the solution is exposed to the direct rays of the sun a crust of silver is separated, and sulphate of ammonia formed.\*

#### 2. Potash-sulphites.

1. Potash-sulphite of suboxide of copper. This substance falls down in the state of a yellow precipitate when nitrate of copper and sulphite of potash are mixed together. It is insoluble in water, and composed, according to Chevreul, of

Sulphited suboxide of copper		•	85.2
Sulphite of potash .	•	•	14.8
			100+
This approaches pretty nearly to			
$4\frac{1}{2}$ atoms sulphited suboxide			<b>58·5</b>
l atom sulphite of potash	•	•	10
	•		68.5

2. Potash-sulphite of silver. Sulphite of silver is soluble in liquid sulphite of potash.

# III. Compound salts of hyposulphurous acid.

## 1. Ammonia-hyposulphites.

1. Ammonia-hyposulphite of silver. This salt is obtained by dissolving chloride of silver in hyposulphite of ammonia, and mixing alcohol with the solution. It is a white salt, very soluble in water, and having an intensely sweet taste. One grain of it communicates a sensible sweetness to 32,000 grains of water. By evaporating the alcoholic solution the same salt is sometimes obtained in thin lengthened hexangular plates. This salt, according to the analysis of Herschell, is composed of

2 atoms hyposulphite of ammonia,

1 atom hyposulphite of silver.

After the hyposulphite of ammonia refuses to dissolve any more chloride of silver, if an additional quantity be added, it is

<sup>\*</sup> Fourcroy. † Ann. de Chim. lxxxiii. 214

rapidly converted into a white crystallized powder. This powder is scarcely soluble in water, but dissolves readily in ammonia, forming an intensely sweet solution, from which an acid throws it down unaltered. Mr. Herschell considers it as a compound of •

1 atom hyposulphite of ammonia, 1 atom hyposulphite of silver.

## 2. Soda-hyposulphites.

1. Soda-hyposulphite of silver. This salt is obtained by dissolving chloride of silver in hyposulphite of soda, and evaporating the solution gently. It crystallizes in thin silky plates, which have an intensely sweet taste, and are readily soluble in water.

#### 3. Strontian-hyposulphites.

1. Strontian-hyposulphite of silver. This salt is formed by the action of hyposulphite of strontian on chloride of silver. It is nearly tasteless and insoluble in water, but dissolves readily in ammonia, and gives to that liquid an intensely sweet taste.\*

### 4. Calcarco-hyposulphites.

1. Calcarco-hyposulphite of silver. This salt is obtained by dissolving chloride of silver in hyposulphite of lime, and mixing the solution with a considerable quantity of alcohol. It is a white salt of an intensely sweet taste, and soluble in water. It is decomposed by a moderate heat.

When more chloride of silver is added to hyposulphite of lime than can be dissolved, the additional portion is converted into a voluminous crystalline powder, of very difficult solubility in water, but abundantly soluble in ammonia, and giving that liquid an intensely sweet taste. Mr. Herschell considers it as a compound of

1 atom hyposulphite of lime, 1 atom hyposulphite of silver.

#### IV. Compound salts of nitric acid.

#### 1. Ammonia-nitrates.

1. Ammonia-nitrate of magnesia. This salt was first de\* Edin. Phil. Jour. i. 27, and 398.

scribed by Fourcroy in 1790. It may be prepared by mixing together the solutions of nitrate of ammonia and nitrate of magnesia, or by decomposing either of these salts in part by the base of the other. When the two salts are mixed together the ammonia-nitrate of magnesia gradually precipitates in crystals.

These crystals are in the form of fine prisms. They have a bitter, acrid, ammoniacal taste. They are soluble at 60° in about 11 parts of water, but boiling water dissolves a greater proportion of them. When exposed to the air they gradually attract moisture, but much more slowly than either of their component parts. The phenomena which this compound exhibits when heated are similar to those which its component parts exhibit in like circumstances.

- 2. Ammonia-nitrate of nickel. This salt, first pointed out by Thenard, is obtained by adding ammonia in excess to the nitrate of nickel. By evaporation a green coloured salt is obtained in crystals. The solution of this salt in water is not rendered turbid by alkalies, but the nickel is thrown down by hydrosulphurets.\*
- 3. Ammonia-nitrate of cobalt. When a solution of cobalt in nitric acid is supersaturated with ammonia, it is well known that no precipitate appears. When this solution is evaporated to dryness, and the residue is treated with water, a red solution is obtained, which yields by slow evaporation regular cubes of a red colour. These crystals are a double salt, composed of nitric acid, ammonia, and oxide of cobalt. They were first observed by Thenard. Their taste is urinous, they are not altered by exposure to the air. When heated they burn with a yellowish-white flame, like nitrate of ammonia, leaving an oxide of cobalt. Their solution in water is neither precipitated by alkalies nor alkaline earths, but when boiled with potash, ammonia is disengaged, and the oxide of cobalt precipitates.†
- 4. Ammonia-nitrated peroxide of tin. The peroxide of tin is insoluble in nitric acid, but it dissolves when treated with nitric acid and ammonia. Hence the reason why a salt containing tin is often procured by the action of nitric acid on tin. Nitrate of ammonia is formed during the process.
  - 5. Ammonia-nitrate of copper. This salt may be obtained

<sup>\*</sup> Ann. de Chim, xliii. 217.

<sup>†</sup> Thenard, Ann. de Chim. xliii. 245.

by adding ammonia to a solution of nitrate of copper. It constitutes a blue crystalline powder, soluble in hot water, and deposited in imperfect crystals as the solution cools. When heated it is decomposed with violence.\*

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- 6. Ammonia-nitrate of mercury. This salt is obtained by mixing concentrated solutions of nitrate of mercury and nitrate of ammonia. The salt is a compound of an atom of each constituent, but its properties have not been examined.
- 7. Ammonia-trisnitrate of mercury. This substance is obtained when nitrate of mercury is decomposed by a slight excess of ammonia. It is a white powder, composed, according to Mitcherlich, of

1 atom nitric acid	•	•	•	6.75
l atom ammonia	•	•	•	2.125
3 atoms oxide of mercury	r	•	•	40.5
			•	49.375

8. Ammonia-nitrate of silver. This salt is obtained by adding ammonia to nitrate of silver. It crystallizes readily, and is very soluble in water. Its constituents, according to the analysis of Mitcherlich, are

Nitric acid	•	•	•	$26 \cdot 4$
Ammonia	•	•	•	18.0
Oxide of silver	•	•	•	<b>55·0</b>
				99.4 ‡
This approaches pretty nea	r			
1 atom nitric acid	•	•	•	6.75
2 atoms ammonia		•	•	4.25
1 atom oxide of silver		•	•	14.75
				25.75

It would seem from this to be a compound of one integrant particle of nitrate of silver, and two integrant particles of ammonia.

#### 2. Soda-nitrates.

1. Soda-subnitrate of platinum. This salt is obtained when nitrated peroxide of platinum is decomposed by soda. A portion of hydrated peroxide first falls. This subsalt when dried is white. §

<sup>\*</sup> Berzelius. ‡ Ann. de Chim. et de Phys. xxxv. 428

<sup>†</sup> Pogenstecher.

Berzelius.

2. Soda-nitrate of rhodium. Dark red crystals, easily soluble in water; but not soluble in alcohol.\*

#### 3. Calcareo-nitrates.

1. Calcareo-nitrate of magnesia. When concentrated solutions of nitrates of lime and of magnesia are mixed together a double salt precipitates which is with difficulty soluble in water. †

# V. Compound salts of carbonic acid.

#### Ammonia-carbonates.

- 1. Ammonia-carbonate of barytes. When ammonia not saturated with carbonic acid is mixed with barytes water, no precipitate falls, nor does it fall if an excess of carbonic acid gas be present. Does this indicate the formation of a double salt, or is it merely a bicarbonate of barytes that remains in solution?
- 2. Ammonia-carbonate of lime. The preceding observations apply also to lime-water and chloride of calcium.
- 3. Ammonia-carbonate of magnesia. When a solution of carbonate of ammonia is mixed cold with sulphate or muriate of magnesia, prismatic crystals are gradually deposited. When heated they leave magnesia. They are scarcely-soluble in a solution of carbonate of ammonia. But when put into water they undergo, according to Bucholz, a gradual decomposition. The constituents of this salt, according to Bucholz, are

Carbonic acid		•	32
Magnesia		•	18
Ammonia and water	•	•	<b>50</b>
		,	
		•	100

According to Guibourt, the magnesia constitutes 15.625 per cent. of the weight of the salt.

- 4. Ammonia-carbonate of glucina. Carbonate of glucina dissolves abundantly in carbonate of ammonia. The colourless solution is decomposed both by heat and by acids.
- 5. Ammonia-carbonate of yttria. Carbonate of yttria likewise dissolves readily in carbonate of ammonia. When the solution is concentrated the double salt precipitates in the state of a white powder. Heat or acids decompose this salt.

<sup>\*</sup> Berzelius. + Bergman. ‡ See Vogel, Ann. de Chim. lxxxix. 128.

- 6. Ammonia-carbonate of zirconia. Carbonate or bicar- Sect. LII. bonate of ammonia dissolves the hydrate of zirconia very slowly and incompletely; but it is a better solvent of the carbonate of zirconia. When the solution is boiled the zirconia is again precipitated in the state of a hydrate.
- 7. Ammonia-carbonated peroxide of iron. The hydrated peroxide of iron dissolves readily in concentrated carbonate of ammonia with a brownish red colour, and is again precipitated when the solution is diluted with water.
- 8. Ammonia-carbonate of copper. Carbonate of copper dissolves in carbonate of ammonia in smaller quantity, and the solution has a lighter colour than the solution of oxide of copper in liquid ammonia.
- 9. Ammonia-carbonate of molybdenum. Hydrated protoxide of molybdenum does not dissolve in pure ammonia or its carbonate. But when an excess of carbonate of ammonia is added to a salt of molybdenum, the precipitate at first thrown down is redissolved, and the liquid assumes a dark brown colour. The precipitate again appears when the liquid is boiled.\*
- 10. Ammonia-carbonated binoxide of molybdenum. hydrated binoxide of molybdenum dissolves in aqueous carbonate of ammonia.+
- 11. Ammonia-carbonate of uranium. The light green precipitate thrown down by carbonate of ammonia from the sulphate of uranium dissolves in an excess of carbonate of ammonia and the solution has a green colour.
- 12. Ammonia-carbonated peroxide of uranium. When newly precipitated carbonated peroxide of uranium is digested in carbonate of ammonia, a fine yellow coloured solution is obtained which deposites rich yellow crystals consisting of four-sided prisms with rectangular bases. This salt is tasteless and insoluble in water. Its constituents, by my analysis, ± are

3 atoms carbonate of ammonia	•	•	14.625
1 atom carbonated peroxide of uranium	n	•	30.75
4 atoms water .		•	4.50
			-
			49.875

13. Ammonia-carbonate of titanic acid. If a solution of titanic acid in an acid be dropt into carbonate of ammonia the precipitate which falls is redissolved. When the liquid is boiled the titanic acid is again precipitated.

#### 2. Potash-carbonates.

1. Potash-carbonate of magnesia. When a solution of bicarbonate of potash is poured into a solution of muriate of magnesia, both in atomic proportions, no precipitate appears at first, but in about 24 hours there is a deposite of irregular crystals in groups, which constitute a compound salt. At first they appear tasteless, but finally leave an alkaline impression. In cold water they fall into powder, bicarbonate of potash dissolves, and carbonate of magnesia remains. When heat is applied, the salt gives out water and becomes opaque. If the heat be increased carbonic acid is given out, and at a red heat a semifusion takes place. From the analysis of Berzelius,\* the constituents of this salt are

1 atom bicarbonate of potash	•	•	11.5
2 atoms carbonate of magnesia	•	•	10.5
9 atoms water	•	•	10.125
			32.125
			02120

- 2. Potash-carbonate of alumina. When carbonate of potash is dropt into a solution of alum, the precipitate which falls, however carefully washed, always retains a quantity of carbonate of potash. The carbonic acid cannot be expelled by heat; but the salt dissolves with effervescence in the stronger acids.
- 3. Potash-carbonate of yttria. Carbonate of yttria dissolves in carbonate of potash, though not quite so easily as in carbonate of ammonia.
- 4. Potash-carbonate of cerium. Protoxide of cerium may be fused with carbonate of potash. The compound dissolves in water with a yellow colour. We may obtain the same compound by dissolving the carbonate of cerium in liquid carbonate of potash.
- 5. Potash-carbonate of peroxide of cerium. Carbonate of potash dissolves some hydrated peroxide of cerium.‡
- 6. Potash-carbonate of zirconia. Hydrated zirconia does not dissolve in carbonate of potash, and carbonate of zirconia very slowly. But when a salt of zirconia is dropt into an excess of carbonate of potash, a solution is instantly effected, and bicarbonate of potash answers better than carbonate. A portion of the zirconia is thrown down by boiling, or by adding ammonia.

The remainder is thrown down when the solution is boiled with sect. LII. sal ammoniac.\*

- 7. Potash-carbonated peroxide of iron. When a salt of peroxide of iron is supersaturated with carbonate of potash, the precipitated hydrate again dissolves with a blood-red colour. It is again thrown down, either by heating or diluting the liquid. Hydrated peroxide of iron is not soluble in a concentrated solution of carbonate of potash. It would appear from this that the presence of the other potash salt contributes to the solution.
- 8. Potash-carbonate of copper. Aqueous bicarbonate of potash dissolves carbonate of copper. The solution has a light blue colour, and, according to Dobereiner, yields octahedral crystals. When oxide of copper and carbonate of potash are fused together, carbonic acid gas is evolved, and we obtain, according to Berzelius, a compound of

1 atom cupreate of potash	•	•	11
3 atoms carbonate of potash	•	•	26.25
			37.95

Water dissolves out the potash and its carbonate, and leaves oxide of copper.

- 9. Potash-carbonate of chromium. Carbonate of chromium dissolves in aqueous carbonate of potash abundantly. The solution has a grass-green colour.
- 10. Potash-carbonate of deutoxide of molybdenum. Newly precipitated hydrate of deutoxide of molybdenum dissolves sparingly in carbonate of potash, and the solution has a yellow colour. When an excess of carbonate of potash is added to a salt of deutoxide of molybdenum, the precipitate, which at first appears is redissolved. By boiling, carbonic acid is given off, and most of the oxide falls, but not the whole. When the solution is exposed to the air, it is speedily converted into molybdate of potash.
- 11. Potash-carbonate of peroxide of uranium. Peroxide of uranium precipitated by carbonate of petash, is soluble in aqueous carbonate or bicarbonate of potash. The solution is yellow, and it deposites a crystalline crust of the double salt. When the crystals are heated to redness they give out water and carbonic acid, and become tile-red, constituting a mixture of carbonate of potash and uraniate of patash.

<sup>\*</sup> Berzelius. + Ibid. • † Chevreul.

12. Potash-carbonated titanic acid. Similar to ammonia-carbonated-titanic acid. The titanic acid is not thrown down by boiling; but it falls if we boil it with a solution of sal ammoniac.

# 3. Soda-carbonates.

- 1. Soda-carbonate of yttria. Carbonate of yttria dissolves in aqueous carbonate of soda. But the earth does not fuse before the blow-pipe with carbonate of soda.\*
- 2. Soda-carbonate of silica. Boiling carbonate of soda dissolves hydrate of silica very abundantly, and allows it to fall, on cooling, in the state of a jelly.
- 3. Soda-carbonate of copper. Similar to potash-carbonate of soda.
- 4. Soda-carbonate of titanic acid. Similar to potash-carbonated titanic acid.
- 5. Soda-carbonate of deutoxide of molybdenum. Similar to potash-carbonate.
- 6. Soda-carbonate of peroxide of molybdenum. When peroxide of uranium precipitated by carbonate of soda is digested in carbonate of soda, it dissolves with a yellow colour.

### 4. Calcareo-carbonates.

1. Calcareo-carbonates of magnesia. This is the mineral known by the names of bitter spar, dolomite, miemite, &c. It is a compound of

1 atom carbonate of lime	•	•	6.25
1 atom carbonate of magnesia	•	•	<b>5·2</b> 5
			11.5

# VI. Compound salts of phosphoric acid.

# 1. Ammonia-phosphates.

1. Ammonia-phosphates of soda. Though this salt, known to chemists by the names of microcosmic salt and fusible salt of urine, was extracted from urine, and examined much sooner than any of the other phosphates, it was long before philosophers were able to form precise notions concerning its nature, or even to obtain it in a state of purity. Margraff was the first who pointed out the method of procuring it pure, and who

<sup>\*</sup> Gahn and Berzelius.

<sup>+</sup> Pfaff, Schweigger's Jour. xxix. 383.

published a detailed description of its properties. He showed that it contained ammonia, and that it yielded phosphorus; but he did not succeed in discovering its whole constituents.\*

It is easily prepared by mixing solutions of the two constituents in the atomic proportions, and concentrating the solution. It crystallizes in fine four-sided pectangular prisms, terminated by rectangular bases. The taste is saline and cooling, and the salt dissolves with facility in water. When heated it melts in its water of crystallization. If the heat be continued the water is dissipated, and in a red heat the ammonia also is disengaged leaving anhydrous biphosphate of soda. The constituents of this salt, according to my analysis, are

1	atom phosphate of ammonia	•	•	6.625
1	atom phosphate of soda	•	•	8.500
19.5	atoms water	•	•	21.9375

37.0625+

It is clear, I think, that there exists another ammonia-phosphate of soda, which contains less water of crystallization, and crystallizes under quite a different form. For Mitcherlich describes the form of the crystal as a doubly oblique rhombic prism, the lateral faces of which are inclined at angles of 38° 44', while the inclination of the base to a side is 93° 4'. form quite different from what I obtained. When 175.56 parts of Mitcherlich's crystals were ignited, the loss of weight was 75.56 parts. While 100 parts of my crystals, treated in the same way, lost 65 parts. Hence Mitcherlich's crystals must be composed of

			<del></del>
10 atoms water	• `	•	11.25
1 atom phosphate of soda	•	•	8.500
I atom phosphate of ammonia	•	•	6.625

26.375

The probability is, that my salt contained just double the quantity of water of crystallization that Mitcherlich's salt did.

2. Ammonia-phosphate of magnesia. This salt occasionally crystallizes in stale urine. In such cases it is transparent and colourless, and the crystals are right rectangular prisms, with square bases. It is formed also when a soluble phosphate and an ammoniacal salt are mixed with a solution of sulphate of It precipitates in the form of a white, tasteless, magnesia.

<sup>\*</sup> Opusc. i. 133.

<sup>&</sup>lt;sup>‡</sup> Ann. de Chim. et de Phys. xix. 400.

insoluble powder; but easily soluble in acetic acid, or muriatic acid. The constituents of this salt, by my analysis, are

1 atom phosphate of ammonia 1 atom phosphate of magnesia			•	6·625 6·5	
4 atoms water	.'	•	•	•	4.5
.•					17:625

Riffault analyzed an ammonia-phosphate of magnesia, which would seem to have contained only half the phosphoric acid in the preceding salt. Its constituents were

1 atom diphospha	ate of a	ammo	onia	•	<b>8·75</b>
1 atom diphospha	ate of	magn	esia	•	9.5
5 atoms water	•	•	•	•	5.625
					23.875

The analysis of Lindbergson coincides with my own.

- 3. Ammonia-phosphate of iron. When ammonia is added to biphosphate of iron, a greenish precipitate falls, soluble in an excess of the precipitant.\*
- 4. Ammonia-phosphated peroxide of iron. White phosphated peroxide of iron dissolves with a brown colour in liquid ammonia. The salt can be again precipitated by evaporation.
- 5. Ammonia-phosphate of nickel. When the solution of phosphate of nickel in ammonia is boiled till no more ammonia is disengaged, this salt falls down in light apple-green flocks.
- 6. Ammonia-phosphate of molybdenum. Phosphate of molybdenum dissolves in liquid ammonia with a dark brown colour.

## 2. Potash-phosphates.

1. Potash-phosphate of soda. This salt was obtained by Mitcherlich by saturating biphosphate of potash with carbonate of soda, and crystallizing the liquid. The crystals are doubly oblique prisms, the lateral faces of which are inclined at angles of 78° 40′, and the base of the prism is inclined to the lateral faces at an angle of 94° 1′, according to Mitcherlich's measurements. The constituents of the salt, according to Mitcherlich, are

<sup>\*</sup> Vogel.

<sup>†</sup> Dobereiner, Schweigger's Jour. xxvi. 271.

<sup>†</sup> Tupputi.

<sup>· §</sup> Berzelius.

1 atom phosphate	of	potash		•	10.5	Sect. LII.
1 atom phosphate	of	soda '	•	•	8.5	
17 atoms water	•	•	•	•	19·125	
					<del></del>	
					<b>8</b> 8·125	

### 3. Calcareo-phosphates.

1. Calcareo-phosphate of peroxide of uranium. This salt occurs native, and is known by the name of uran mica. From Berzelius's analysis, it is a compound of

2 atoms phosphated peroxide of uranium						65.5	
1 atom subsesqui	phosp	hate o	of lime	•		9.75	
12 atoms water	•	•	•	•	•	13.5	
						88 <b>·75</b>	

# 4. Magnesia-phosphates.

1. Magnesia-phosphate of nickel. When a solution of oxide of nickel and of magnesia containing phosphoric acid is precipitated by ammonia, this salt falls down.\*

## 5. Ferro-phosphates.

1. Ferro-phosphate of manganese. The mineral called triplite, is a compound of

1 atom diphosphate of iron .	•	13.5
l atom diphosphate of manganese	•	13.5
		97

## VII. Compound salts of phosphorous acid.

## 1. Ammonia-phosphites.

1. Ammonia-phosphite of magnesia. Obtained by mixing together solutions of the two constituents in the atomic proportions. It crystallizes, and is slightly soluble in water.†

# VIII. Compound salts of arsenic acid.

## 1. Ammonia-arseniates.

1. Ammonia-arseniate of soda. This salt is obtained by

<sup>\*</sup> Rose. + Fourcroy and Vauquelin.

mixing the two constituents together in the atomic proportions, and concentrating the solution. The crystals, according to Mitcherlich, have the same shape as those of ammonia-phosphate of soda, with a minimum of water. The constituents of the salt are

1	atom arseniate	of	amm	onia		•	9.375
1	atom arseniate	of	soda			•	11.25
10	atoms water	•	•	•	•	•	11.25
							31.875*

#### 2. Potash-arseniates.

1. Potash-arseniate of soda. Obtained by neutralizing binarseniate of potash by carbonate of soda, and concentrating the solution. The crystals have the same form and characters as those of potash-phosphate of soda. The composition, according to the analysis of Mitcherlich, is similar, being

1 atom arseniate of pota	ash	•	13.25
1 atom arseniate of soda	a		11.25
17 atoms water .	•	•	19·125
•			43.625

# IX. Compound salts of silicic acid.

#### 1. Potash-silicates.

1. Potash-silicate of barytes. When barytes water is mixed with a solution of silicate of potash, this salt is precipitated. It would appear, from Dalton's observations, that it is a compound of

I atom disilicate of potash	•	14
1 atom disilicate of barytes	•	21
		35

2. Potash-silicate of lime. Formed in the same way as the preceding salt, which it doubtless resembles in its composition.

# X. Compound salts of chromic acid.

1. Potash-chromates.

# -

1. Potash-chromate of soda. This salt is easily formed by

\* Ann. de Chim. et de Phys. xix. 399.

neutralizing bichromate of potash with carbonate of soda, and Sect. LL concentrating the solution. It is deposited in beautiful yellow crystals, which seem to be four-sided oblique prisms. When heated, they decrepitate and become red; but recover their colour on cooling. They are composed of

1 atom chromate of potash 1 atom chromate of soda	•	12·5 10·5
		23

with about half an atom of water, probably only mechanically lodged between the plates of the crystals.\*

2. Potash-chromate of magnesia. Obtained by digesting a solution of bichromate of potash over carbonate of magnesia till the salt becomes yellow, and is fully saturated. When the liquid is concentrated, a crust of the double salt is deposited at the bottom of the vessel. It is composed of a congeries of small hard crystals, so closely compacted, that it is scarce possible to recognise the shape. The colour is a fine yellow, and the salt is not altered by exposure to the air. The taste is bitter and unpleasant. The salt is pretty soluble in water. When heated, it becomes red; and it retains that colour, though with a strong tint of yellow, after it has become cold. In a strong red heat, it fuses and effervesces, as if a gas was making its escape. The colour becomes brown, and the salt is no longer completely soluble. Its constituents, by my analysis, are

1 atom chromate of potas	h.	12.5
1 atom chromate of magn	iesia .	$9 \cdot 0$
2 atoms water .		2.25
		23.75+

# XI. Compound salts of tungstic acid.

# 1. Ammonia-tungstate.

1. Ammonia-tungstate of molybdenum. When ammonia is dropt into an aqueous solution of tungstate of deutoxide of molybdenum, the liquid becomes colourless, and after some time a white powder is deposited, which is insoluble in water, and from which soda separates deutoxide of molybdenum.

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* Phil. Trans. 1827, p. 223.
                                     † Ibid. p. 224.
                                                             1 Berzelius.
II.
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# XII. Compound salts of oxalic acid.

#### 1. Ammonia-oxalates.

- 1. Ammonia-oxalate of potash. When binoxalate of potash is saturated with ammonia, and the solution concentrated, the double salt shoots into needles, which are not altered by exposure to the air.\*
- 2. Ammonia-oxalate of magnesia. When solutions of muriate of magnesia and oxalate of ammonia are mixed together and concentrated, this double salt is gradually deposited, constituting a white, translucent, imperfectly crystallized, and tasteless crust. It requires more than 480 times its weight of water to dissolve it. This double salt was first examined by Brandes, who found its constituents to be

Oxalic acid	•	•	<b>5</b> 8
Ammonia	•	•	9
Magnesia	•	•	<b>25</b>
Water	•	•	8
			100+

This corresponds with

3.04 atoms oxalic acid,

1 atom ammonia,

2.36 atoms magnesia,

1.68 atoms water.

If we allow for an excess of  $\frac{1}{3}$  atom of magnesia, which is very likely to be an error in the analysis, from the great difficulty of obtaining magnesia in a state of purity, the above analysis leads to the conclusion, that the true constituents of this salt are

1	atom oxalate of ammonia					6.625	
2	atoms oxalate of magnesia					14	
18	atoms water			•	•	1.875	
•						22:500	

- 3. Ammonia-oxalate of peroxide of iron. A yellow insoluble powder.
- 4. Ammonia-oxalate of cobalt. Oxalate of cobalt dissolves in a concentrated solution of carbonate of ammonia. The solution has a crimson-red colour, and is not precipitated by exposure to the air.

<sup>\*</sup> Wenzel.

- 5. Ammonia-oxalate of nickel. Oxalate of ammonia dissolves Sect. L11. oxalate of nickel, and when the solution is concentrated, the double salt is deposited in green coloured prisms.\*
- 6. Ammonia-oxalate of copper. Of this salt there are three species, all of which were first examined and analyzed by Vogel of Bayreuth.
- (1.) The neutral salt. This salt was obtained by mixing together a solution of oxalate of ammonia and oxalate of copper, and digesting the mixture. The oxalate of copper soon dissolved, and, by evaporation, small crystals were deposited in the form of rhomboidal plates. These crystals constitute the salt in question. They are not altered by exposure to the atmosphere. They are insoluble in water, but are gradually decomposed by that liquid. When heated, they give out water, and afterwards ammonia. When suddenly heated, they detonate loudly, and leave oxide of copper. The constituents of this salt, according to Vogel's analysis, are

l atom oxalate o	f ammo	nia		6.625
l atom oxalate o	f copper	r	•	9.5
3 atoms water	.•	•	•	<b>3</b> ·3 <b>75</b>

19.5

(2.) The subsalt. If oxalate of copper be put into caustic ammonia, and agitated till as much of it be dissolved as can be taken up by the cold liquid, and the liquid be then poured into a flat dish, it gradually deposites dark sky-blue crystals, composed of flat six-sided prisms, having two broad and four narrow faces. These crystals speedily effloresce when exposed to the air, and not only water but ammonia likewise is disengaged from it. The loss which it sustains by efflorescing is 18 per cent., and it loses no weight even when exposed to the heat of boiling water. According to the analysis of Vogel, assisted, however, by some calculation, the constituents of this salt are as follows:

1 atom dioxalate of ammonia	٠. ١	8.75
1 atom dioxalate of copper	•	14.5
2 atoms water	•	2.25
		95.5

(3.) Subsesquisalt. If a greater quantity of oxalate of copper be put into caustic ammonia than the alkali is capable of

<sup>\*</sup> Tupputi.

dissolving, the oxalate of copper is gradually changed into a sandy powder, very similar in its appearance to smalt. This powder is the salt in question. It is not altered by exposure to the air, nor by a heat sufficient to deprive the first subspecies of its water of crystallization. When more strongly heated, the ammonia is driven off, and the residue burns with flame like the two preceding subspecies. Its constituents, as determined by Vogel by experiments, aided by a little calculation, are as follows:\*

Oxalic acid	•		•	•	43.00
Ammonia	•		•	•	9.72
Peroxide of	copp	er		•	45.58
Water .	•		•	•	1.70

100.00

Allowing the water to be only mechanically lodged in the interstices of the salt, the constituents are obviously

l atom ammonia .	•	•	2.125
2 atoms oxide of copper			10
2 atoms oxalic acid	•	•	9
			21.125

or in the ratio of 1 atom acid to 2 atoms base.

### 2. Potash-oxalates.

- 1. Potash-oxalate of soda. When binoxalate of potash is saturated with soda, and the solution concentrated, it deposites crystals in octahedrons, easily soluble in water, and efflorescing when exposed to the air.+
- 2. Potash-oxalate of alumina. Binoxalate of potash dissolves hydrate of alumina, and forms a gummy mass, remaining dry in the air, and easily soluble in water.
- 3. Potash-oxalate of yttria. An insoluble white powder, which when ignited leaves a mixture of yttria and carbonate of potash.§
- 4. Potash-oxalate of cerium. A white powder, insoluble in water, and leaving, after ignition, a mixture of protoxide of cerium and carbonate of potash.
- 5. Potash-oxal te of peroxide of iron. Obtained by mixing permuriate of iron with an excess of oxalate of potash. The

<sup>\*</sup> Schweigger's Journal, vii. 35. † Wenzel. ‡ Ibid. \$ Berzelius. † Ibid.

solution deposites small, oblique, four-sided prisms, of an apple- Sect. LII. green colour. The taste is sweet and inky, and the salt dissolves easily in water, with a light yellowish-green colour.\*

- Binoxalate of potash, when 6. Potash-oxalate of lead. digested on oxide of lead, dissolves a portion, and deposites the double salt in small needles+
- 7. Potash-oxalate of copper. When binoxalate of potash is digested on carbonate of copper, a dark sky-blue solution is obtained, which when evaporated deposites crystals distinguished by two different forms. Some of them were needleform crystals, which speedily effloresced in the air. consisted chiefly of long, slender, six-sided prisms. The remaining crystals are oblique parallelopipedons with rhomboidal ends much larger than the lateral faces. These crystals have a greener colour than the first kind, and are not altered by exposure to the atmosphere. From the analysis of Vogel, of Bayreuth, it appears that these two species of salt differ from each other solely in the proportion of their water of crystallization; the first kind containing 4 atoms water, and the second only 2 atoms.

The needle-form crystals are composed of

1 atom oxalate	of po	tash	•	10.5
1 atom exalate	of co	pper	•	9.5
•4 atoms water	•	•	•	4.5
				94.5

While the constituents of the oblique prisms are

1 atom oxalate of potash	•	10.5
1 atom oxalate of copper	٠	9.5
2 atoms water	•	$2 \cdot 25$

22.25

- 8. Potash-oxalate of suboxide of mercury. Binoxalate of potash dissolves suboxide of mercury, and the solution deposites the double salt in oblique prisms.§
- 9. Potash-oxalate of silver. Binoxalate of potash dissolves oxide of silver, and the solution deposites rhomboidal crystals, not altered by exposure to the air, and easily soluble in water.
- 10. Potash-oxalate of deutoxide of molybdenum. Obtained by dissolving deutoxide of molybdenum in binoxalate of potash. The salt is soluble in water.¶
  - · Bucholz, Gehlen's Jour. (2d series), ix. 679. + Wenzel. ‡ Schweigger's Jour. ii. 435. § Wenzel. • | Ibid. ¶ Berzelius.

- 11. Potash-oxalate of molybdic acid. Binoxalate of potash dissolves molybdic acid readily, but the double salt does not crystallize.\*
- 12. Potash-oxalate of antimony. When equal weights of glass of antimony and oxalate of potash are digested in water and the solution repeatedly crystallized, white needles are obtained, agglutinated in stars. They have a slightly styptic and metallic taste, and at 50° dissolve in  $9\frac{1}{2}$  times their weight of water. They contain 20·19 per cent. of water of crystallization, and possess the emetic properties of tartar emetic.†

### 3. Soda-Oxalates.

1. Soda-oxalate of copper. Vogel of Bayreuth prepared this salt by saturating binoxalate of potash with soda, and pouring a saturated solution of sulphate of copper into the liquid. pulverulent precipitate fell, which was redissolved by agitation. On evaporating the liquid, the triple oxalate of potash and copper first crystallized. Afterwards crystals of soda-oxalate of copper were deposited. These crystals have a dark skyblue colour. They are needle-form or feather-shaped, and consist of four-sided prisms, sometimes with all the sides equal, sometimes with two broad and two narrow sides. They are not altered by exposure to the air, at least they neither effloresce nor deliquesce; but they gradually become green, and then dark brown, without any other apparent alteration; and this change takes place very speedily in the sun's rays. It is insoluble in water without decomposition. According to the analysis of Vogel, the constituents of this salt are as follows:

l atom oxalate of soda	•	•	8.5
1 atom oxalate of copper	•	•	9.5
2 atoms water	•	•	2.25
			20.25

## XIII. Compound salts of acetic acid.

### 1. Ammonia-acetates.

- 1. Ammonia-acetate of copper. Obtained by dissolving acetate of copper in aqueous ammonia and gentle evaporation.
  - \* Berzelius. † Lassaigne, Jour. Chem. Med. iii. 278.

<sup>‡</sup> Schweigger's Journal vii. 21.

Small blue crystals are deposited, smelling of acetic acid, and efflorescing when exposed to the air.\*

#### 2. Soda-acetates.

1. Soda-acetate of rhodium. A red coloured salt, easily soluble in water, but not in alcohol.†

### 3. Calcareo-acetates.

1. Calcareo-acetate of copper. This salt was prepared about 12 years ago by Messrs. Turnbull and Ramsay of Glasgow, for the calico-printers, who probably used it as a resist paste. It has a fine deep blue colour, is translucent, and crystallized in six-sided prisms. It is readily soluble in water, and has the usual disagreeable cupreous taste which distinguishes the salts of copper. Its constituents, according to my analysis, are

l atom acetat	e of	lim	e	•	•	9.75
1 atom acetat	e of	cop	per			11.25
6 atoms water			•	•	•	6.75
						***************************************
						27·75.±

## XIV. Compound salts of mellitic acid.

1. Potash-mellate of silver. When mellate of potash acidulated with nitric acid and nitrate of silver are mixed together no precipitate falls; but after some time small brilliant translucent crystals are deposited. They are six-sided prisms, having two of the angles 121° 30′ and four 119° 11′. It is evident from this that the primary form is a right oblique prism, the faces of which are inclined at angles of 121° 30′ and 58° 30′. The acute edges are replaced by tangent planes, which would make the four new edges 119° 15′, instead of 119° 11′, as measured by Wöhler. When these crystals are heated they first lose water, become opaque, and then swell up with a kind of detonation, and leave a long twisted matter, composed of silver and carbonate of potash.§

# XV. Compound salts of tartaric acid.

### 1. Ammonia-tartrates.

- 1. Ammonia-tartrate of potash. This salt was known many
  - \* Coulon, Ann. de Chim. xcvi. 327.

+ Berzelius.

† First Principles, ii. 449.

§ Wöhler, Poggendorf's Annalen, vii. 333

years ago, and is mentioned by Macquer. It is easily formed by saturating bitartrate of potash with ammonia and crystallizing the solution. The crystals are at first transparent, and are square prisms terminated by two faces set on two opposite angles of the prism, and meeting at an angle of 135°. It is easily soluble in water. When exposed to the air it effloresces, loses its ammonia, and is converted into bitartrate of potash. This double salt, by my analysis, is composed of

1 atom tartrate of ammonia	•	•	10.375
1 atom tartrate of potash .	•	•	14.250
2 atoms water			2.25

26.875.

2. Ammonia-tartrate of lime. The aqueous solution of bitartrate of lime is not precipitated by ammonia.\*

#### 2. Potash-tartrates.

These are very numerous on account of the many experiments made with bitartrate of potash, which was long considered by chemists as an acid.

1. Potash-tartrate of soda. This salt is usually prepared by putting one part of tartar in five parts of boiling water, and adding gradually carbonate of soda in powder as long as it continues to produce an effervescence. The tartar gradually dissolves. When the saturation is complete, the solution is filtered and evaporated to the consistence of a syrup. On cooling, the tartrate of potash-and-soda crystallizes.

This salt has been distinguished by the name of salt of seignette, or Rochelle salt, because it was first formed and introduced into medicine by Mr. Seignette, an apothecary at Rochelle. This gentleman recommended it in a tract published in 1672. It was soon after introduced into practice in Paris by Lemery; and, becoming a fashionable medicine, made the fortune of the discoverer. For some time its composition was kept secret; but Boulduc and Geoffroy discovered its component parts in 1731.

This salt crystallizes in prisms of eight, or ten, or twelve unequal sides, having their ends truncated at right angles. They are generally divided into two in the direction of their axes; and the base on which they stand is marked with two diagonal lines, so as to divide it into four triangles. The

primary form is a right rhombic prism, whose faces meet at Sect. LII. angles of 100° and 80°. Sometimes the edges are replaced by tangent planes, sometimes by two, and sometimes by three planes.\* The taste of the salt is bitter. According to Osan, its solubility in water is as follows:

1 part of salt at 37° dissolves in 3·3 parts water 52° 2.4 75° 1.5

According to Brandes

1 part of salt at 42° dissolves in 2 parts water

54°₽ 1.2 770 0.4299°± 0.3

Sulphuric or tartaric acid occasions a precipitate of cream of tartar, when dropt into the solution of this salt. The specific gravity of the crystals is 1.756.† Its constituents, according to the analysis of Schulze, are

1 atom tartrate of potash	•	•	14.25
1 atom tartrate of soda		•	$12 \cdot 25$
10 atoms water	•	•	11.25

37.75

I have sometimes analyzed crystals of the salt having ten atoms water; but in general the water amounts only to eight atoms, making the atomic weight of the salt 35.5.‡

- 2. Potash-tartrate of lithia. When the excess of acid in the bitartrate of potash is neutralized by boiling the salt with carbonate of lithia, and the salt is left to spontaneous evaporation, we obtain large crystals, consisting of rectangular four-sided prisms, whose bases are rectangles. The diagonals of these rectangles are distinctly marked, and the four triangles thus produced are streaked parallel to the sides of the rectangle. This remarkable appearance is permanent, and may therefore constitute a good character of lithia. This salt dissolves readily in water. It has a salt taste, without any bitterness, and is scarcely altered by exposure to the air.§
- 3. Potash-tartrate of barytes. When bitartrate of potash is saturated with barytes water, no precipitate falls.
  - \* Brooke, Annals of Philosophy (2d series), v. 451.
  - + Watson's Chemical Essays, v. 67. ‡ First Principles, ii. 439.
  - § Gmelin, Gilbert's Annalen, lix. p. 417.
  - W Thenard.

- 4. Potash-tartrate of strontian. Bitartrate of potash is not precipitated by strontian water.\*
- 5. Potash-tartrate of lime. When solutions of tartar and lime water are mixed, this salt falls. Tartrate of potash boiled on tartrate of lime, dissolves 27 per cent. of it. When concentrated to the consistence of a syrup many needles make their appearance which redissolve on the application of heat. By evaporation to dryness, a transparent matter is obtained which attracts moisture when exposed to the air, and dissolves completely in hot water. But when cold water is used almost all the tartrate of lime separates.

When tartrate of lime is digested in an aqueous solution of potash it is dissolved. The solution is liquid and caustic. Carbonate of potash when dropped into it throws down all the lime. When the saturated solution is diluted with water a portion of the tartrate of lime is precipitated. By heat it is converted into a clammy mass, which when filtered hot leaves a quantity of subsesquitrate of lime. The cold liquid seems to be a solution of tartrate of lime in potash. By heat the potash takes away a portion of the tartaric acid and lets a subsesquisalt fall. On cooling the lime again recovers the acid it had lost and the whole is redissolved.†

6. Potash-tartrate of magnesia. This salt may be formed by boiling a mixture of tartar and magnesia in water, and leaving the liquid to spontaneous evaporation. The crystals are white and opaque, and seem small rhomboids, tasteless and insoluble in water. From an analysis of 2 grains of the salt I deduced its constituents as follows:

1 atom bitartrate	of potash	•	22.5
2 atoms tartrate	of magnesia	•	21.5
4 atoms water	• •	•	4.5

48.5

7. Potash-tartrate of alumina. This salt may be obtained by dissolving hydrate of alumina in bitartrate of potash. A gummy-like mass is obtained, which is not precipitated from its solution by alkalies.

Tartrate of potash when assisted by heat dissolves a good deal of hydrate of alumina without becoming alkaline.

8. Potash-tartrate of iron. This salt may be obtained by

<sup>\*</sup> Thenard.

<sup>†</sup> Lassone, Crell's Chem. Jour. iv. 109; Osan, Kastner's Arch. iii. 204.

digesting 4 parts of tartar in one part of iron filings with a sufficient quantity of water. When the solution is sufficiently concentrated it deposites greenish white needles having a disagreeable taste, little soluble in water, and not precipitated by alkalies or their carbonates.\*

- 9. Potash-tartrated peroxide of iron. This salt was formerly called tartarised tincture of Mars, chalybeated tartar, and tartarised iron. It is obtained by a large digestion of the preceding salt in contact with the air. Or still better by dissolving peroxide of iron in aqueous tartar. The solution is yellowish-brown, it does not crystallize, acts as an alkali, and has a sweetish and inky taste. The dry salt dissolves in four times its weight of water, and is also slightly soluble in alcohol.+
- 10. Potash-tartrate of manganese. Obtained by dissolving carbonate of manganese in aqueous tartar. The salt crystallizes with difficulty, is very soluble in water, and is not precipitated by alkalies or their carbonates. ±
- 11. Potash-tartrate of cobalt. When solutions of the two constituents are mixed and concentrated, the double salt crystallizes in large rhomboids.
- 12. Potash-tartrate of nickel. Obtained by boiling tartar and oxide of nickel with a sufficient quantity of water. not crystallize, has a sweet taste, and is very soluble in water.
- 13. Potash-tartrate of zinc. This salt may be formed by boiling together tartar and zinc filings and water. It is very soluble in water, and not easily crystallized. No precipitation is produced in its solution by the alkalies or their carbonates. ||
- 14. Potash-tartrate of lead. Obtained by boiling a mixture of tartar and oxide of lead. It is an insoluble white powder. It is not decomposed by alkalies nor sulphuric acid. ¶
- 15. Potash-tartrate of tin. This salt may be formed by boiling together tartar and the oxide of tin in water. very soluble, and therefore its solution crystallizes with difficulty. No precipitate is produced in it by the alkalies or their carbonates. \*\*
- 16. Potash-tartrate of copper. This salt may be formed by boiling together oxide of copper and tartar in water. solution yields by evaporation blue crystals, which have a sweetish taste, and contain a great proportion of metal.++ When tartar and copper, or its oxides, are boiled together, they

<sup>\*</sup> Thenard. † Bucholz. ‡ Scheele.

<sup>||</sup> Dijon Academicians, and Thenard, Ann. de Chim. xxxviii, 35.

<sup>\*\*</sup> Ibid. Ann. de Chim. xxxviii. 35. ¶ Thenard. ++ Ibid. 36.

dissolve, and by evaporating to dryness a bluish green powder is obtained, which, according to Leonardi, constitutes the better kind of the pigment called *Brunswich green.*\*

- 17. Potash-tartrate of suboxide of mercury. Tartrate of potash precipitates nitrated suboxide of mercury. The white, scaly salt, when exposed to the light, becomes yellow. It is little soluble in water. By potash (in consequence of the formation of a double salt) it is only half decomposed.
- 18. Potash-tartrate of mercury. When 6 parts of tartar and 1 part of red oxide of mercury are boiled together small crystals (according to Monnet) are deposited.
- 19. Potash-tartrate of silver. A white insoluble powder. This salt is decomposed by the alkalies and their carbonates, and by the sulphates and muriates.+
- 20. Potash-tartrate of molybdenum. A solution of molybdic acid in tartar is digested with zinc. The molybdic acid is converted into deutoxide, and muriatic acid being dropped in and the whole digested for a considerable time the molybdenum is reduced to the state of protoxide, and the double salt falls down in the state of a black powder. When ignited in an open crucible it leaves molybdate of potash. The salt dissolves slowly in water with a purple colour, and abundantly in liquid ammonia with a deep purple colour. By evaporation the double salt again falls down.
- 21. Potash-tartrated deutoxide of molybdenum. When tartar is digested with an excess of hydrated deutoxide of molybdenum there is formed a brown powder difficultly soluble in water, but easily soluble in alkalies. The solution of this salt in water seems to be neutral, while the residual portion is a subsalt.§
- 22. Potash-tartrate of molybdic acid. When tartar and molybdic acid (previously ignited) are boiled together in water, a solution is obtained, which by evaporation leaves a gummy like matter, constituting the double salt.
- 23. Potash-tartrate of antimony. This salt, usually denominated tartar emetic, is much more employed in this country as a medicine than all the other antimonial preparations put together. It was first made known by Adrian de Mynsicht in his Thesaurus Medico-Chymicus, published in 1631. But the preparation was in all probability suggested by a treatise, en-

<sup>\*</sup> Gren's Handbuch der Chimie, iii. 331. † Ann. de Chim. xxviii. 36. † Berzelius. † Ibid.

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titled Methodus in Pulverem, published in Italy in 1620. This book, written by Dr. Cornachinus, gives an account of the method of preparing a powder which had been invented by Dudley, Earl of Warwick, and which had acquired great celebrity in Italy, in consequence of the wonderful cures which it had performed. This powder was composed of scammony, sulphuret of antimony, and tartar, triturated together. The extraordinary effects which it produced would naturally draw the attention of chemists to the combination of antimonial preparations with tartar.

Tartar emetic was first prepared by boiling together tartar and the *crocus metallorum*,\* as it was called, in water, filtering the solution, and evaporating it till it yields crystals; glass of antimony was afterwards substituted for the crocus. But it would be needless to enumerate the various methods which have been adopted according to the fancy of different operators. These methods have been collected by Bergman, and are described by him in his treatise on *Antimoniated Tartar*.† The processes followed in London may be seen in Mr. Phillips' *Experimental Examination of the Pharmacopæa Londinensis*, p. 58.

At present, the glass of antimony, or the protoxide of antimony, are usually employed. Either of these is mixed with its own weight of tartar, and the mixture boiled in 10 or 12 parts of water, till the tartar be saturated. The solution is then filtered and evaporated till a pellicle forms on its surface. On cooling it deposites regular crystals of tartar emetic. Thenard has observed, that there always remains in the solution a quantity of uncombined tartrate of potash, it ought not therefore to be evaporated too far, otherwise the crystals of that salt will mix with those of the tartar emetic.‡

Tartar emetic has a white colour, and crystallizes in rhombic octahedrons. When exposed to the air it becomes opaque and effloresces on the surface, but does not fall to powder. Its specific gravity is 2.8946. Its solubility in water of different temperatures, as determined by Brandes, is as follows:

<sup>\*</sup> An impure hydrosulphuret, formed by detonating in a crucible equal weights of sulphuret of antimony and nitre, and washing the residuum in water till the liquid comes off tasteless.

<sup>†</sup> Opusc. i. 338. ‡ Ann. de Chim. xxxviii. 39.

<sup>§</sup> See a description of the crystal by Brooke, Annals of Philosophy (2d series), vi. 41.

Class	ı.
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1

part salt at 4	7°2 dissolves	in 19	parts	water.
-	0	12.6	-	
8	88	8.2		
9	9.5	7·1		
12	<b>2</b>	5.6		
14	4.5	4.8		
16	7	$3\cdot 2$		
18	9.5	3		
21	<b>2</b>	2.8		

According to Phillips, when strongly heated it loses 7.38 per cent. of water. When heated to redness in close vessels it leaves a very combustible pyrophorus. Sulphuretted hydrogen gas throws down all the antimony and leaves a solution of bitartrate of potash. According to Wallquist iron alone of the metals throws down the whole antimony from this salt. taric acid throws down tartar from it. Ammonia produces a slight precipitate, but carbonate of ammonia is without action. Potash does not precipitate the dilute solution, but carbonate of potash throws down almost all the antimony. When 1 part of tartar emetic dissolved in 480 of water is mixed with lime water, some tartrate of lime and tartrate of antimony falls, but no precipitate appears when the solution is more dilute. analyzed this salt by dissolving 50 grains of it in water, and throwing down the antimony by sulphuretted hydrogen gas. I obtained 24.59 grains of sesquisulphuret of antimony, equivalent to 21.23 protoxide of antimony. The residual liquid being evaporated gave 28.69 grains of tartar. Hence the constituents are

Protox Bitartr				•	•	21·23 28·69
Loss	•	•	•	•	•	49·92 0·08
						<del></del>

50

From the analysis of bitartrate of potash given in a preceding part of this chapter, it is obvious that 28.69 bitartrate of potash are equivalent to

Tartaric a	acid	•	•	19.12
Potash	•	•	•	6.95
Water	•	•	•	2.62

Resolving these weights into atoms, we have the constituents Sect. LII. of the salt:

1.997 atom tartaric acid

1.92 atom protoxide of antimony

1 atom potash

2.139 atoms water.

The loss sustained in the analysis was chiefly protoxide of antimony—a little having attached itself to the inside of a glass tube. These numbers approach so near the following that we can have no doubt about the constitution of the salt being

2 atoms tartaric a	cid	•	•	•	•	16.5
2 atoms protoxide	e of a	ntimon	ıy	•	•	19
l atom potash	•	•	•	•	•	6
2 atoms water	•	•	•	•	•	$2 \cdot 25$
						<del></del>
						<b>43·75</b>
We may therefore	consid	ler tar	tar er	netic a	as con	aposed of
l atom tartrate of	potas	sh		•	•	14.25
1 atom ditartrate			7	•	•	27.25
2 atoms water	•		•	•	•	2.25
						***************************************
						43.75

Mr. Phillips has endeavoured to demonstrate that the quantity of water in tartar emetic is three atoms.\* In the specimen which I analyzed, and which was opaque in consequence of long exposure to the atmosphere, the water was certainly only two atoms. But it is by no means improbable that, in newly prepared crystals, there may be an additional atom, which gradually makes its escape when the salt is left exposed to the atmosphere.

- 24. Potash-tartrate of antimonic acid. When four parts tartar are digested over peroxide of antimony two parts of it are dissolved. The solution has a saline and sweetish taste, and by slow evaporation gives a crystalline, tough, yellowish white matter, easily soluble in water.†
- 25. Potash-tartrate of chromium. This salt may be obtained by digesting tartar and green oxide of chromium with a sufficient quantity of water. A deep blue solution is obtained, having a sweet and acidulous taste when evaporated to dryness, and a black and almost tasteless powder remains. But it may be again dissolved in water and a blue sweet solution

<sup>\*</sup> Annals of Philosophy (2d series), ix. 372. † Geiger.

obtained as at first. This solution is not precipitated by alkalies. I found this salt to be accompound of

1 atom tartrate of	potas	h 🔻	•	•	14.25
1 atom tartrate of	chron	nium	t. •	•	13.25
2 atoms water	•	•	•	•	2.25
		(			29.75*

#### 3. Soda-tartrates.

- 1. Soda-tartrate of lithia. Obtained in the same way as potash-tartrate of lithia. It forms long four-sided rectangular prisms, often terminated by an oblique face. It dissolves readily in water. Its taste is saline and weak, and it undergoes little alteration when left exposed to the air.+
- 2. Soda-tartrate of barytes. This salt precipitates when solutions of seignette salt and muriate of barytes are mixed, while muriate of potash remains in solution. When the solution is very dilute the precipitate falls in needles, and only after some days. The salt is scarcely soluble in water, but it dissolves better in seignette salt and in muriate of barytes. ‡
- 3. Soda-tartrate of lime. When solutions of seignette salt and muriate of lime are mixed together, small white grains precipitate, or if the liquid be dilute, many small needles are deposited. These constitute the double salt. They are very little soluble in water, but dissolve readily in solution of seignette salt.§

An aqueous solution of four soda dissolves, when assisted by heat, 13 of tartrate of lime. The hydrate of lime is dissolved by aqueous tartrate of soda. These solutions become thicker the oftener they are heated, and are at last converted to a stiff jelly. When too much diluted the solution does not become thick. Subtartrate of lime is deposited when heat is applied. This precipitate is again dissolved when the liquid becomes cold, and the more rapidly the more dilute it is. By evaporating to dryness a white mass is obtained.

4. Soda-tartrate of copper. Bitartrate of copper dissolves readily in a solution of soda.

# 4. Barytes-tartrates.

- 1. Barytes-tartrate of antimony. Obtained by precipitating
- Phil. Trans. 1827, p. 216.
- † Gmelin, Gilbert's Annalen, lix. p. 414.
- ‡ Kaiser.
- § Ibid. Repert. xxii. 260.

Osann.

¶ Thenard.

tartar emetic by a barytes salt. Its constituents are in the sect LII. same proportions as those in tartar emetic, substituting barytes for potash.\*

### 5. Calcareo-tartrates.

1. Calcareo-tartrate of antimony. Similar in its formation and constitution to the preceding salt.

## 6. Argento-tartrates.

1. Argento-tartrate of antimony. Obtained by precipitating tartar emetic by nitrate of silver. Its constituents, as determined by the analysis of Wallquist, are

I atom tartra	ate of sil	ver	•	•	•	23
1 atom ditart		intimo	ony	•	•	27.25
2 atoms water	er .		•	•	• >	2.25
		•				
						50.5

Thus its constitution is the same as that of tartar emetic, substituting oxide of silver for potash.

## XVI. Compound salts of vinic acid.

Ammonia-vinate of peroxide of iron. Vinated peroxide of iron, when mixed with ammonia, remains clear, and when concentrated deposites grains of a brownish yellow colour easily soluble in water, and emitting the smell of ammonia when treated with potash. †

## XVII. Compound salts of mallic acid.

#### 1. Ammonia-malates.

- 1. Ammonia-malate of lime. Obtained by saturating a supermalate of lime with ammonia. It crystallizes in the form of bimalate of lime, though the salt contains but little lime.‡
- 2. Ammonia-malate of zinc. When ammonia is added to malate of zinc only a portion of the zinc is deposited, in consequence of the formation of a double salt.§
- 3. Ammonia-malate of lead. Obtained when malate of lead is decomposed by ammonia. It is soluble and may be crystallized. ||

#### 2. Potash-malates.

1. Potash-malate of lime. When potash is added to the

\* Wallquist. + Walchner. † Braconnot. § Ibid. I Ibid. 3 F II.

milk-warm solution of malate of lime two double salts are formed, one of which precipitates, while the other remains in solution.\*

#### 3. Soda-malates.

1. Soda-malate of lime. Carbonate of soda renders the solution of bimalate of lime muddy, even while hot.+

#### 4. Zinc-malates.

1. Zinc-malate of lead. This salt precipitates when malate of lead and acetate of lead are mixed together.;

# XVIII. Compound salts of butyric acid.

1. Barytes-butyrate of lime. When aqueous solutions of two butyrate of lime and three butyrate of barytes are mixed together and left to spontaneous evaporation, they deposite octahedrons, which at 64° dissolve in 3.8 times their weight of water. 100 parts of the crystals decomposed by sulphuric acid leave 68 parts of sulphuric acid salts. §

## XIX. Compound salts with two acids.

## 1. Sulphuric acid.

1. Sulpho-chromate of potash. This salt was obtained by mixing together solutions of three integrant particles of chromate of potash and one integrant particle of sulphate of potash and concentrating the solution. Greenish yellow crystals are deposited in octahedrons, or double four-sided pyramids, with a four-sided square prism interposed between them. The crystals are transparent, have a saline and bitter taste, and are very soluble in water. When heated to redness the salt becomes opaque, but loses no weight. It is therefore anhydrous, and is composed, according to my analysis, of

2. Sulpho-chromate of glucina. When sulphate of glucina is poured into chromic acid the appearance of the solution is not altered; but when the liquid is evaporated there remains

behind a double salt in dendritical crystals in a state of efflo- Sect LII.
rescence.\*

3. Sulpho-acetate of soda. This salt was obtained by Mr. Mill by mixing together 200 grains of acetate of lime dried at the temperature of 430° with 400 grains of crystals of sulphate of soda both dissolved in water. The whole lime was separated and by evaporation a double salt was obtained in crystals. Mr. Mill has not given a description of the salt, but found it, by analysis, a compound of

7 atoms acetate of soda 1 atom sulphate of soda

Both retaining their water of crystallization.+

#### 2. Nitric acid.

- 1. Nitro-phosphate of barytes. When nitrate of barytes and phosphate of ammonia are mixed this double salt falls in the state of a gelatinous precipitate. When washed with water nitric acid is dissolved and phosphate of barytes remains in the state of a white powder ‡
- 2. Nitro-phosphate of lead. When phosphoric acid is added to a solution of nitrate of lead, or when a solution of phosphate of lead in nitric is concentrated, small crystalline grains are precipitated, which, according to the analysis of Berzelius, are composed of

The nitrate of lead is easily washed away by hot water. When the salt is heated nitrous acid is driven off, and subsesquiphosphate of lead remains.

3. Nitro-tungstate of potash. This salt is obtained in the form of a white powder; it has an acid and bitter taste, reddens the infusion of turnsole, and is soluble in 20 parts of boiling water. The De Luyarts first showed it to be a compound of nitric acid, oxide of tungsten, and potash.

#### 3. Carbonic acid.

- 1. Carbo-phosphate of soda. I give this name to a salt which appeared in the prussiate of potash leys in Mr. Macin-
  - \* John, Annals of Philosophy, iv. 425.
  - † Annals of Philosophy (2d. series), x. 113. 

    ‡ Berzelius.
  - § Ibid., Ann. de Chim. et de Phys. ii. 161.

tosh's manufactory at Campsie, when cracknales were substituted for the hoofs of cattle in the mixture burnt for the formation of prussic acid. It was in pretty regular six-sided prisms, which had a cooling and alkaline taste, and gave a violet colour to cudbear paper. They were pretty soluble in water, and not altered by exposure to the air. They effervesced slightly, but distinctly, in nitric acid. My analysis of this salt, when corrected by substituting the true atomic weight of phosphoric acid, gives the constituents of this salt as follows:

1	atom carbonate of soda	•	•	6.75
3	atoms phosphate of soda	•	•	25.50
<b>4</b> 0	atoms water	•	•	45.00
				77.95

2. Carbo-tartrate of soda and alumina. When solutions of tartrate of alumina and carbonate of soda each in the atomic proportions are mixed no precipitate falls; but when the solution is left to spontaneous evaporation a transparent colourless salt gradually forms in long four-sided prisms. These crystals do not affect litmus or cudbear paper. They have a disagreeable taste, bearing some resemblance to that of sulphate of zinc. The constituents of this double salt are

1 atom carbonate of soda			•	•	··6·75	
1 atom tartrate o	f alum	ina -		•	10.5	
9 atoms water	•	•	•	•	10.125	
		•			27.375+	

#### 4. Titanic acid.

1. Titanio-silicate of potash. This compound remains behind when titanic acid is mixed with an excess of silica and carbonate of potash and ignited, and the mass afterwards washed with water, to separate the carbonate and silicate of potash. While moist it dissolves readily in concentrated muriatic acid, and when the solution is boiled and concentrated it becomes covered with a crust. Ammonia throws down a mixture of titanic acid and silica, from which muriatic acid dissolves out the titanic acid, leaving the silica.

### 5. Boracic acid.

1. Boro-tartrate of potash. This curious compound, the
\* First Principles, ii. 451. + Ibid. + H. Rose.

tartarus boraxatus of some chemists, is obtained by boiling tar- Sect. LIL tar and boracic acid for a long time in water. Soubeiran conceives that the boracic acid acts the part of a base, and saturates the second atom of tartaric acid in the tartar. But as the salt still retains its acid properties, this explanation is not so prob-Four parts of tartar, and one of crystallized boracic acid, constitute 4.5 parts of the dry salt. It has a very sour taste, and when ignited, leaves boracic acid and carbonate of potash. It dissolves in 3ths of its weight of cold, and in 1th of its weight of boiling water. The solution deposites no tartar; but on cooling, becomes a gelatinous, transparent mass, which contains 0.34 water. The aqueous solution of 4 parts tartar, and 0.5 part of anhydrous boracic acid, when left to evaporate under a glass containing quicklime, deposites white rhomboidal crystals, which have a very sour taste. When decomposed by the Voltaic pile, they deposite tartar at the positive pole, and boracic acid, with some tartaric acid, at the negative pole. The dried salt dissolves in twice its weight of boiling water, and slightly in weak alcohol; but not in concentrated alcohol.

- 2. Boro-tartrate of soda. Bitartrate of soda and borax when mixed together mutually dissolve into a gummy, not crystallizable salt, which deliquesces in the air.\*
- 3. Boro-tartrate of ammonia and potash. Obtained by mixing two parts of tartar with one part of borate of ammonia. A gummy mass, having a sour taste.+
- 4. Boro-tartrate of potash-and-soda. This is the salt which has a place in most of the German Pharmacopæias under the name of cremor tartari solubilis, and tartras potassæ boraxatus. It is made by dissolving one part of borax in eight parts of boiling water, and adding three parts of tartar, or as much as it is capable of dissolving. The compound thus prepared is used in dropsy, amenorrhoea, &c. and possesses nearly the same virtues as cream-of-tartar. It is a transparent, viscid mass, which may be dried, and then reduced to powder. Its colour is yellowish; it has a cooling, bitter, and sour taste, more disagreeable than that of tartar. When exposed to the air it deliquesces. It is soluble in its own weight of cold, and in half its weight of boiling water. I find that this salt when dried weighs precisely as much as its two constituents. Hence both salts retain their water. I have found it composed of

Class I.	1 atom biborate of soda .	10
	2 atoms bitartrate of potash	22.5
,	12 atoms water	13.5

And doubtless the two salts might be combined in other proportions.

## XX. Combinations of ummonia with anhydrous salts.

It has been long known that several salts have the property of absorbing ammoniacal gas in definite proportions, of increasing much in bulk and falling to powder, and of again giving out the gas without alteration. M. H. Rose has lately generalized this observation, and shown that it holds in a great number of salts. His method was to render the salts anhydrous, and then to leave them exposed to an atmosphere of dry ammoniacal gas till they refused to absorb any more. It will be sufficient if we give here a table of the anhydrous salts tried, and the proportion of ammonia with which they united.

1.	1	atom sulphate of mangar	nese	•	9.5
	2	atoms ammonia .	•	•	4.25
2.	1	atom sulphate of zinc	. 19	•	10.25
	$2\frac{1}{2}$	atoms ammonia .	•	•	5.3125
					15.5625
3.		atom sulphate of copper	•	•	10
	$2rac{1}{2}$	atoms ammonia .	•	•	5.3125
		•			15.3125

Berzelius formed a similar compound with hydrous sulphate of copper. It was composed of

	1 atom sulphate of copper	•	•	10
	2 atoms ammonia .	•	•	4.25
	l atom water	•	•	1.125
	•			15.375
4.	l atom sulphate of nickel	•	•	9.25
	3 atoms ammonia .	•	•	6.375
				15.625

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ANHYDROUS COMBINATION			
5. 1 atom sulphate of cobalt 3 atoms ammonia .	•	•	9:2 <i>E</i> 6:375
			15.625
6. 1 atom sulphate of cadmium 3 atoms ammonia .	<b>,•</b>	•	13 6·375
			19.375
7. l atom sulphate of silver l atom ammonia	•	•	19·75 2·125
•			21.875
8. 1 atom nitrate of silver	•		21.5
3 atoms ammonia .	•	•	6.375
			27.875
9. 1 atom chloride of calcium	•	•	7
4 atoms ammonia .	•	•	8.5
			15.5
0. 1 atom chloride of strontium 4 atoms ammonia .		•	10 8·5
• atoms ammonia .	•	•	
			18.5
<ol> <li>1 atom chloride of copper</li> <li>3 atoms ammonia</li> </ol>	•	•	8·5 6·375
			14.875
2. 1 atom chloride of nickel			7.75
3 atoms ammonia .	•	•	6.375
			14.125
3. 1 atom chloride of cobalt	•	•	7.75
2 atoms ammonia .	•	•	2.25
			10
4. 1 atom chloride of lead	•	•	17.5
0.75 atom ammonia	•	•	1.595
			19.095

Class 11.	15. l 'atom chloride of silver $l_{\frac{1}{2}}$ atom ammonia	18·25 3·1875
		21.4375
	16. I atom subchloride of mercury 1 atom ammonia	29·5 2·125
		31.625
	17. 1 atom chloride of mercury . 0.5 atom ammonia	17 1·0625
		18.0625
	18. 1 atom chloride of antimony 1 atom ammonia	12·5 2·125
		14.625
	19. 1 atom bromide of mercury . 0.5 atom ammonia	22·5 1·0625
		23.5625
	20. I atom iodide of mercury	28·25 2·125
		30.375
	21. 1 atom cyanodide of mercury . 1 atom ammonia	15·75 2·125
		17.875*

### CLASS II.

#### CHLORINE SALTS.

Chlorine, like oxygen, combines with all the acidifiable bases, and doubtless forms acids with many of them; but, except muriatic acid, or hydrochloric acid, scarcely any of the salts of chlorine have been investigated. M. Bonsdorf, indeed, has lately began the investigation of some other genera of

<sup>\*</sup> See Poggendorf's Annalen, xx. 147.

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chlorine salts, and has shown that the chloride of mercury is capable of acting the part of an acid, and combining with a variety of chlorine bases. The same observation applies to the chloride of platinum, of gold, and of palladium. I propose in the subsequent section to give an account of those chlorine salts which have been hitherto examined. This branch of chemistry is destined hereafter to acquire a much greater extent than it has yet reached, and may probably at length vie in importance with the class of oxygen salts itself.

### SECTION I .-- OF MURIATES AND CHLORIDES.

The chemical law is, that whatever principle has converted the acidifiable base into an acid, the same principle must have converted the alkalifiable base into an alkali. Oxygen acids unite only with oxygen bases, and chlorine acids with chlorides. When a chlorine acid is united to an oxide, a double decomposition usually takes place, water being formed, and a chloride. Muriates, therefore, must consist of muriatic acid, united to a chloride. But such salts, supposing them to exist, have not yet been investigated. Most of those salts usually called muriates, are really chlorides. Whether they are all so, has not yet been determined.

1. Muriate of ammonia, or sal ammoniac. This salt has been in common use for several centuries; but I am not aware of any evidence that the ancients were acquainted with it. Tournforte appears to have known its constituents in 1700. Geoffroy, junior, pointed them out experimentally in 1716 and 1723, as was afterwards done by Duhamel more precisely in 1735.\* For many years the manufacture was confined to Egypt. About 1760, a manufacture of it was established in Edinburgh by Dr. Hutton and Mr. Davy, and about the same time various others arose both in this country and on the continent. It was made by extracting sulphate of ammonia from This salt was mixed with common salt, and subjected to heat in large globular glass vessels, the sal ammoniac sublimed, and was obtained in a cake at the upper part of the vessel. There remained unsublimed sulphate of soda, which was crystallized, and exported to the continent in large quantities. During the French revolutionary war, a tax was laid upon the sulphate of soda. This, by raising the price, put an end to the sale of the salt, and destroyed almost all the sal ammoniac manufactories in Great Britain.

<sup>\*</sup> See Mem. Paris for these years.

Sal ammoniac is a white translucent salt, having a saline and somewhat bitter taste. It crystallizes in regular octahedrons. Its specific gravity, as determined by Dr. Watson, is 1.450. A saturated solution at 50° has a specific gravity 1.072. The crystals at 50° dissolve in 2.727 times their weight of water.\* Wenzel found it soluble in 2.24 parts of water of the temperature  $144.5^{\circ}$ .† A hundred parts of alcohol of the strength 0.834 dissolve  $1\frac{1}{2}$  of this salt.

In its common form (which is an opaque mass) this salt is not much affected by the air, but its crystals are liable to deliquesce.

When heated, it sublimes without decomposition in the form of a white smoke, which exhales a peculiar odour.

When this salt is sublimed with gold leaf, there is found in the neck of the retort an amethyst coloured matter, bordering on purple, soluble in water, and forming a purple solution. When filtered, there remains behind a purple powder. This salt seems from this to be capable of oxidizing gold.‡

It is formed when equal volumes of ammoniacal and muriatic acid gases are mixed together. Hence it consists obviously of

1 atom muriatic acid . 4.625 1 atom ammonia . 2.125

6.75

Some chemists consider it as a compound of 1 atom chlorine and 1 atom ammonium. By ammonium is understood a hypothetic metal, composed of 1 atom of azote and 4 atoms of hydrogen. Of course, the atomic constitution of the salt according to both views is the same; but it would be difficult to conceive a reason why the atom of hydrogen previously united to chlorine, should leave that substance in order to unite with azote, to which 3 atoms of hydrogen are already united.

2. Chloride of potassium. This salt has been long known. It was at first distinguished by the name of febrifuge, or digestive salt of Sylvius, because it was employed by De le Boé Sylvius, the celebrated founder of Iatro chemistry, as a remedy in fevers. Boerhaave called it regenerated sea salt, because in his time the difference between potash and soda was not understood. The French chemists gave it the name of muriate of potash, which it retained till its real nature was pointed out

<sup>\*</sup> Gren's Handbuch, i. 488. † Verwandtschaft, 309.

<sup>‡</sup> Storr, Crell's New Biscoveries, &c. part ii. p. 41.

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by Sir H. Davy. It is easily obtained by saturating carbonate of potash with muriatic acid, and concentrating the solution. The crystals are right rectangular prisms, with square bases.

It is white, and has a taste very similar to that of common salt. Its specific gravity, as determined by Kirwan, is 1.836. At 32°, 100 parts of water dissolve 29.23 parts of this salt, and for every 1°.8 above 32° the water takes up 0.2738 more of the salt. When heated it decrepitates, and at a red heat melts into a liquid without undergoing decomposition. 97.76 grains of the crystals by ignition lose 2.76 grains of weight, which is moisture. 8.75 grains of anhydrous carbonate of soda saturated with muriatic acid and ignited leave exactly 9.5 grains of this salt. Hence, it is obvious that it is a chloride composed of

3. Chloride of sodium. This salt, usually called common, or sea, or rock salt, and by the French chemists muriate of soda, has been known and employed as an indispensable seasoner of food since the very origin of the human race. Vast beds of it exist in the new red sandstone formation, and sea water contains about 3.5 per cent. of it, from which it is easily procured by evaporating that liquid. It was known as early as the time of Geber that muriatic acid could be obtained from it, and Stahl in his Specimen Becherianum, affirmed that its base is an alkali. But it was Duhamel who first pointed out the method of obtaining this base in a separate state, and who showed in what respects it differed from potash. The true nature of the salt was first pointed out by Davy.

This salt is white. It crystallizes in cubes, and sometimes, though rarely, in octahedrons. Its taste is well known, and is what we usually denominate salt. Its specific gravity, as determined by Fahrenheit, is 2·125.\* Mohs found it 2·257. According to Gay-Lussac, it is rather more soluble in water at 32° than at 57°. According to him its solubility at different temperatures is as follows:

100 water at 57° dissolve 36 parts of salt.

 $\begin{array}{ccc} 140 & 37 \\ 229\frac{1}{2} & 40.38 \end{array}$ 

<sup>\*</sup> Phil. Trans. 1724, p. 114.

When heated it decrepitates, and at a red heat melts into a liquid without undergoing decomposition. In a high temperature it may be sublimed. It contains no water of crystallization, but is a compound of

4. Chloride of lithium. It is easily obtained by saturating carbonate of lithia with muriatic acid, evaporating the solution to dryness, redissolving, and crystallizing. The crystals are cubes, and the taste very similar to that of common salt. The salt speedily deliquesces into a liquid when exposed to the air. When heated to redness it fuses, and in a white heat may be sublimed. It contains no water of crystallization, and is a compound of

1 atom chlorine . . 4.51 atom lithium . . 0.75

5. Chloride of barium. This salt is easily obtained by dissolving carbonate of barytes in muriatic acid and crystallizing the solution.\* The crystals are usually short prisms with square bases, or at least only slightly oblique. The crystals are commonly tables. They are described by Crawford as sometimes constituting pyramidal dodecahedrons. The taste is pungent and disagreeable, and, like the other preparations of barytes, the salt is poisonous. Its solubility at different temperatures, as determined by Brandes and Melm,+ is as follows:

100 water at 61° dissolve 39.6 of this salt.

42.2
43.7
51
<b>65</b>
48
63
<b>65</b>
<b>72</b>
. <b>7</b> 8‡

<sup>\*</sup> It is usually made, I suspect, in London, from the native carbonate of barytes from Anglesark. This is probably the reason why it contains always a little lead.

<sup>†</sup> Repert. xiv. 97.

<sup>+</sup> Gay-Lussac.

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Absolute alcohol does not dissolve it while cold, but at a boiling heat it dissolves about  $\frac{1}{400}$ th of its weight of it.\* I find it to be sensibly soluble in alcohol of the specific gravity 0.808. It is not altered by exposure to the air. When heated it decrepitates, but does not liquefy. At a high temperature it may be fused, but we cannot decompose it by heat. The constituents of this salt in crystals are

1 atom chlorine	•	•	4.5
1 atom barium	•	•	8.5
2 atoms water	•	•	2.25

15.25

By ignition the water is driven off, but if we expose the anhydrous salt to the air it exactly recovers its original weight by absorbing water.

6. Chloride of strontian. This salt is easily formed by dissolving carbonate of strontian in muriatic acid and concentrating the solution till it crystallizes. The crystals are very long needles consisting most commonly of six-sided prisms, two opposite faces of which are much larger than the other four. Some of the prisms have the aspect of regular hexagonals. Water at the temperature of 60° dissolves  $1\frac{1}{2}$  times its weight of this salt. Boiling water dissolves any quantity whatever. According to Bucholz, it is soluble at 60° in 24 times its weight of absolute alcohol, and in 19 times its weight of boiling alcohol.† The alcoholic solution burns with a beautiful red flame, especially when stirred. The crystals slowly deliquesce in a moist atmosphere. When heated they undergo the watery fusion, and then are reduced to a white powder. In a strong red heat it melts into a liquid. Its constituents, by my analysis, are

1	atom chlorine		•	•	4.5
1	atom strontian		•	•	5.5
9	atoms water	•	•	•	10.125
					20.125

7. Chloride of calcium. This salt was formerly called fixed ammoniac, because it was usually obtained by decomposing sal ammoniac by means of lime. The French chemists gave it the name of muriate of lime. It is easily obtained by dissolving carbonate of lime in muriatic acid and concentrating

<sup>\*</sup> Bucholz, Beitrage, iii. 24.

the solution till it deposites crystals. It is somewhat difficult to obtain it in regular crystals. The form is the regular six-sided prism, usually striated longitudinally. When 4 parts of the salt are dissolved in 1 part of water at 70°, and the solution exposed to the air at 32°, the crystals speedily form. The taste is very bitter and pungent, and when exposed to the air it speedily deliquesces. It is exceedingly soluble in water. At 32°, 1 part of water dissolves 2 of the salt; at 60°, 1 part water dissolves 4 parts of the salt, and boiling water dissolves any quantity of it whatever. 'When the evaporation of a solution is carried on till its specific gravity is 1.450 it crystallizes when exposed to an atmosphere of 32°. If its specific gravity at 80° be as high as 1.490 it assumes on cooling the form of a hard pearl coloured mass.\* It dissolves in great quantity in alcohol, even when anhydrous. When heated it melts in its water of crystallization, and is then gradually changed into a white matter which may be fused at a rcd heat, during which a portion of the chlorine is usually dissipated. When thus treated it has the property of shining in the dark, and was on that account called phosphorus of Homberg, who first discovered the fact.

> The constituents of this salt in crystals, by my analysis, are as follows:

1 atom chlorine		•	4.5
1 atom calcium	•	•	2.5
7 atoms water	•	•	7.875
•			14.075

8. Chloride of magnesium. This salt exists in several springs, particularly that of Lymington, in Hampshire. It was first described by Mr. Brown in the Philosophical Transactions for 1723,† but its nature was not understood till the experiments of Black and Margraff had established the peculiar nature of its base. It may be formed by dissolving magnesia or its carbonate in muriatic acid, and evaporating the solution to the proper consistency. It is not easily crystallized; but I have obtained it from a manufacturer of Epsom salt in pretty large four-sided prisms, with bases very nearly square. These crystals deliquesce when exposed to the air.

The taste of this salt is bitter, hot, and biting. 100 parts of it dissolve in 60 parts of cold, and 27.3 parts of hot water.

It dissolves in 5 times its weight of alcohol, of the specific gra-

<sup>\*</sup> Walker, Nicholson's Jour. v. 226. + Vol. xxxii. p. 348.

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vity 0.90, and in twice its weight of alcohol of the specific gravity 0.817.\* When heated it liquefies in its water of crystallization, then is converted into a white mass, and in a red heat loses a considerable portion of acid, a great deal of magnesia remaining in an uncombined state. When thrown into water after being thus heated, it hisses like a red-hot iron, much heat is evolved, and the undecomposed portion dissolves. The constituents of this salt, by my analysis, are

1 atom chlorine	•	•	4.5
I atom magnesium .	• •	•	1.5
6 atoms water	•	•	6.75
			10.75

9. Chloride of aluminum. This salt has been described in Vol. I. p. 452 of this work. When this chloride is dissolved in water, or when alumina is dissolved directly in muriatic acid, and the solution cautiously evaporated to dryness, we obtain a beautiful white matter without any appearance of crystallization. Its taste is astringent and acid, and it reddens vegetable blues. It deliquesces in the air. It dissolves in about the fourth part of its weight of water. Pure alcohol, at the temperature of the atmosphere, dissolves half its weight of it, and when boiling it takes up two-thirds of its weight, but again deposites a portion as the liquid cools.

When this salt is heated it loses all its water and acid, and nothing remains but pure alumina. We have no evidence, therefore, that it is any thing else than muriate of alumina. Its constituents, by my analysis, are

l atom muriatic acid	•	•	4.625
l atom alumina	•	•	2.25
3 atoms water	•	•	3.375

10.25

Bucholz+ gives as the analysis of a muriate of alumina, which seems to have been a dimuriate, and to have contained twice the quantity of water stated above. It seems to have been composed of

•	•	4.628
•	•	4.5
•	•	6.75
	•	· · ·

15.875

<sup>\*</sup> Kirwan on Mineral Waters, p. 274.

<sup>†</sup> Beitrage, iii. 111.

10. Chloride of glucinum, described in vol. I. p. 459.

When chloride of glucinum is dissolved in water, or when glucina is dissolved directly in muriatic acid, we obtain by evaporation a salt in crystals, which, when heated, loses its water and acid, while pure glucina remains. Hence it is probably a muriate of glucina. From the experiments of Vauquelin and Berzelius, it would appear that muriatic acid and glucina unite in three different proportions.

- (1.) Bimuriate which crystallizes, is soluble in water and alcohol, and does not deliqueses.
- (2.) Muriate, obtained by evaporating the solution of the preceding salt, and driving off the water and excess of acid. It is a gummy matter which does not crystallize.
- (3.) Dimuriate which precipitates during the evaporation of the bimuriate.
  - 11. Chloride of yttrium, described in vol. I. p. 463.

When it is dissolved in water, or when yttria is directly dissolved in muriatic acid, a muriate of yttria is obtained.

The solution when carefully concentrated crystallizes in large right prisms, having two of the opposite edges replaced by tangent planes, so as to form a six-sided prism. It has a sweet and astringent taste, and is very deliquescent. When heated it undergoes the watery fusion, and at a red heat the acid is driven off, and pure yttria remains. The constituents of this salt, according to the analysis of Dr. Steel, in my laboratory, are

1 atom muriatic acid	•	•	4.625
1 atom yttria	•	•	5.5
3 atoms water	•	•	3.375
			13.5

- 12. Chlorides of cerium, described in vol. I. p. 468.
- 13. Chloride of zirconium is formed by heating zirconium in chlorine gas.

When it is dissolved in water, or when hydrate of zirconia is dissolved in muriatic acid, and the solution sufficiently concentrated, muriate of zirconia is deposited in small white silky needles of an astringent taste. When exposed to the air they become opaque, and lose half their water. A strong heat drives off all the water and acid, leaving the zirconia. This salt dissolves readily in water and alcohol, but scarcely in muriatic acid.

When evaporated to dryness at the temperature of 140°, it

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loses half its acid, and is converted into a dimuriate which is a white matter, dissolving very slowly, but completely in water. When the solution is long boiled most of the zirconia falls in a white gelatinous matter, which, when dry, assumes a glassy appearance. It still retains a portion of acid.\*

14. Chloride of thorium. This salt has been mentioned in vol. I. p. 476 of this work. No description of its properties has been yet published.

Hydrated thorina dissolves in muriatic acid, and by evaporation a fibrous mass is obtained, but it does not crystallize nor dry when exposed to the air. In a strong heat it loses its acid, and thorina remains.+

15. Chloride of iron described in vol. I. p. 492. When it is dissolved in water, or when iron is directly dissolved in muriatic acid, and the solution sufficiently concentrated, crystals are deposited which have a light green colour, and consist of rhomboidal plates with bevelled edges. Hence the form of the crystalis an octahedron composed of two four-sided pyramids with a rhombic base. The apices of the pyramids are truncated so deep as to convert the crystal into a table. The taste is sweet and astringent. When exposed to the air they soon deliquesce and become yellow and opaque from the absorption of oxygen. They dissolve readily in water and alcohol. When heated they undergo the aqueous fusion. They absorb, when in solution, deutoxide of azote still more abundantly than sulphate of iron. The constituents of this salt, by my analysis, are

1 atom chlorine	•	•	4.5
1 atom iron	•	•	3.5
4 atoms water	•	•	4.5
•			19.5

16. Sesquichloride of iron. Described in vol. I. p. 492.

When the sesquichloride of iron is dissolved in water or when hydrated peroxide of iron is dissolved in muriatic acid, a deep brown solution is obtained. Its odour is peculiar, and its taste, even when much diluted with water, is exceedingly astringent. When evaporated to dryness, it yields an uncrystallizable orange-coloured mass, which deliquesces in the air, and is soluble in alcohol. This salt gives a yellow tinge to animal and vegetable substances, as is the case with chlorine. When sulphuric acid is poured upon it, the odour of chlorine is perceptible. This salt does not absorb nitrous gas. When

<sup>\*</sup> Berzelius.

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sulphuretted hydrogen gas is made to pass through it, part of the oxygen is abstracted, and the salt is converted into muriate of iron.\*

When this salt is distilled, chlorine passes over, and the iron is reduced to the state of black oxide. This gas is also formed and exhaled during the solution of red oxide of iron in muriatic acid, at least if the solution be promoted by the application of heat.

If the heat be increased after the sesquimuriate of iron is evaporated to dryness, the wkqle salt sublimes, not however in the state of sesquimuriate, but of simple muriate, which is capable of crystallizing.

According to Stein, when the solution of sesquichloride of iron is carefully evaporated, it deposites aurora-red tables, which deliquesce in the air, and dissolve readily in water and alcohol.

17. Chloride of manganese. Described in vol. I. p. 522.

When this chloride is dissolved in water, or when carbonate of manganese is dissolved in muriatic acid, and the solution carefully concentrated, beautiful flesh coloured crystals are deposited, consisting of short six-sided prisms, two of the opposite sides of which are much larger than the other four. The taste of these crystals has some resemblance to that of sulphate of soda. It is very soluble both in water and alcohol, and deliquesces rapidly when exposed to the air. The specific gravity, according to John, is 1.56. The constituents of this salt, according to my analysis, are as follows:

1 atom chlorine	•	•	4.5
l atom manganese	•	•	$3 \cdot 5$
5 atoms water	•	•	<b>5·62</b> 5

13.625

- 18. Muriated sesquioxide of manganese. When the sesquioxide of manganese is digested in muriatic acid without the application of heat, a brown coloured solution is obtained. This solution cannot be concentrated by heat without losing its colour, and being converted into the preceding salt. When kept it gradually loses its colour without any application of heat. Of course the properties of this solution have not hitherto been accurately determined.
- 19. Chloride of nickel. When carbonate of nickel is dissolved in muriatic acid, and the solution sufficiently concentrated, beautiful green crystals are deposited. They are four-

<sup>\*</sup> Davy, Journal of the Royal Institution, p. 181.

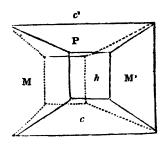
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sided prisms, but so indistinctly crystallized, that the exact dimensions cannot be made out. They deliquesce when exposed to the air. They dissolve in  $1\frac{1}{2}$  or twice their weight of cold water. They are soluble also in alcohol. When heated the water may be drawn off, while chloride of nickel remains. The constituents of this salt, by my analysis, are

1 atom chlorine	• .	•	4.5
l atom nickel	•	•	3.25
6 atoms water		•	6.75

14.5

20. Chloride of cobalt. Described in vol. I. p. 540. When this chloride is dissolved in water, or when carbonate of cobalt is dissolved in muriatic acid, and the solution properly concentrated, it deposites garnet coloured crystals, which consist of oblique rhombic prisms, as figured in the mar-



gin. The following are the measurements of the angles of this prism, as determined by Mr. Brooke.\*

P on M or M'	•	•	109° 31
$\mathbf{P}$ on $h$	•	•	122 20
P on $c'$	•	•	106 20
$\lambda$ on $c$	•	•	131 20
M on h	•	•	128 40
M on $M'$		•	<b>77 20</b>

They dissolve readily in water. When heated they undergo the watery fusion, and when the water is dissipated they assume a deep blue colour. If we continue the heat in close vessels the whole water is drawn off and a small blue chloride remains, which readily dissolves in water with a red colour. When the solution of this salt is dilute, it has a red colour, but when very much concentrated, the colour becomes blue; or green, if iron or nickel be present in the liquid. This solution constitutes the sympathetic ink of Hellot. It was first made known by Waitz in 1705;† it was described a second time by Teichmeyer in 1731;‡ and a third time by Hellot in 1737.§ The cause of this singular change of colour has not hitherto been explained

<sup>\*</sup> Annals of Philosophy (2d series), vii. 365.

<sup>†</sup> See Wiegleb's Geschichte, i. 126. 

‡ Commerc. Literarum, p. 91.

<sup>§</sup> Mem. Par. 1737.

in a satisfactory manner. But it is easy to show that the disappearing of the colour is owing to the absorption of moisture from the atmosphere. For the green colour is permanent if the paper be confined under the receiver of an air-pump along with a flat vessel filled with concentrated sulphuric acid.

The constituents of this salt, by my analysis, are as follows:

1 atom chlorine		•	•	4.5
1 atom cobalt		•	•	3.25
5 atoms water	4	•	•	5.625
				10.075

21. Chloride of zinc. Described in vol. I. p. 548.

Muriatic acid dissolves zinc with facility; but the solution cannot be made to crystallize. When kept upon the sandbath till it ceases to lose weight, it concretes on cooling into a white opaque mass, having a strong and disagreeable taste, and speedily deliquescing when exposed to the air. It is easily soluble in water. Its constituents, by my analysis, are

1 atom chlorine	•	•	4.5
1 atom zinc	•	•	4.25
1 atom water	•	•	1.125
në.			9.875

The water may be driven off, and the chloride obtained in an anhydrous state.

22. Chloride of cadmium. Described in vol. I. p. 555.

Cadmium dissolves readily in muriatic acid. The solution, by spontaneous evaporation, is gradually converted into a mass of short satiny crystals, somewhat resembling asbestus. This salt, by my analysis, is composed of

1 atom chlorine	•	•	4.5
1 atom cadmium		•	7.0
2 atoms water	•	•	2.25
			19.75

By heat the water may be driven off, and the chlorine obtained in an anhydrous state.

23. Chloride of lead. Described in vol. I. p. 563.

The crystals are said to be six-sided prisms. But I have obtained them in flat four-sided prisms with an oblique summit.

24. Proto-chloride of tin. Described in vol. I. p. 557.

When tin is dissolved in muriatic acid, which it is in large quantities for the use of the calico-printers, the solution yields

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large crystals. They are white, and have something of the diamond lustre. The shape is an oblique four-sided prism, with one edge usually replaced by a tangent plane. The termination is a bihedral summit, consisting of two faces proceeding from the two opposite entire corners of the prism. These crystals are translucent. They strongly redden vegetable blues. The taste is acid, and very acrid and disagreeable. Specific gravity 2.656. When put into water the crystals leave a little hydrate of protoxide of tin unacted on. When heated the salt melts and flows like nitrate of silver, quite transparent and colourless. It then boils up and becomes dry, and a white matter remains, which dissolves in water. The salt is also soluble in alcohol. In oil of turpentine it becomes yellow and opaque, but does not dissolve. These crystals were not altered by a week's exposure to the air. Their constituents, according to my analysis, are

1 atom chlorine		•	•	4.5
l atom tin		•	•	7.25
3 atoms water	•	•	•	3.375

15.125

From the experiments of Proust, confirmed by those of Dr. John Davy, it appears that when potash in small quantity is added to the solution of the preceding salt, a white precipitate falls, which is a subsalt containing only half the tin which exists in the crystals.

25. Perchloride of tin. Described in Vol. I. p. 575.

In a paper inserted in the Edinburgh Philosophical Transactions, I described crystals of this salt in needles seemingly right four-sided prisms. These crystals did not dissolve in water except partially. When heated they melted, boiled, became yellow, fused, and were volatilized, excepting a small residue. I considered these crystals as composed of

					14.625
2 3	atom	water .		•	0.75
1	atom	peroxide of tin		•	9.25
1	atom	muriatic acid .	•		4.625

But I have since obtained this salt in a more perfect state, and have found that it contains a great deal of protoxide of tin, though from the rapidity with which the tin is peroxidized, it is difficult to say how much.

I have also got crystals in broad plates from the same manufactory. They have a silky lustre, and deliquesce rapidly when exposed to the air. They contain both oxides of tin, though the quantity of protoxide is considerably less than that of peroxide. It would appear from this that the two chlorides of tin are capable of combining in more than one proportion. It is probable that the crystal's of perchloride of tin are composed of

2 atoms chlorine	е	•	•	9
1 atom tin	• .	•	•	7.25
5 atoms water	•	•	•	5.625

21.875

26. Dichloride of copper. Described in Vol. I. p. 593.

27. Chloride of copper. Described in Vol. I. p. 594.

When this chloride is dissolved in water, if the solution be concentrated, the salt is deposited in rectangular prisms of a fine grass green colour. This salt is exceedingly acrid and caustic. Its specific gravity is 1.6776.\* It is very soluble in water, and when exposed to the air very soon attracts moisture, and is converted into a liquid of the consistence of oil. At a moderate heat it melts, and assumes a solid form when cold. Its composition is as follows:

1 atom chlorine	•	•	4.5
1 atom copper	•	•	<b>4</b> ,
3 atoms water		•	3.375

11.875

28. Chloride of bismuth. Described in Vol. I. p. 607.

Bismuth may be readily dissolved in muriatic acid when assisted by a little nitric acid. The solution when properly concentrated yields small prismatic crystals, which when sublimed become butter of bismuth. When diluted with water they undergo decomposition, a subsalt precipitating and a supersalt remaining in solution. The subsalt when heated fuses without undergoing decomposition.

- 29. Chloride of mercury. Described in Vol. I. p. 616.
- 30. Dichloride of mercury. Described in Vol. I. p. 618.
- 31. Chloride of silver. Described in Vol. I. p. 631.
- 32. Sesquichloride of gold.
- 33. Chloride of gold.
- 34. Dichloride of gold.

Described in Vol. I. p. 644.

<sup>\*</sup> Hassenfratz, Ann. de Chim. xxviii. 12.

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- 35. Chloride of platinum. 36. Bichloride of platinum. 36. Bescribed in Vol. I. p. 663.
- 37. Chlorides of iridium. Described in Vol. I. p. 689.
- 38. Chlorides of osmium. Described in Vol. I. p. 697.
- 39. Chloride of tellurium. Described in Vol. I. p. 298.

Tellurium dissolves in muriatic acid. The solution is colourless. Water throws down from it a subsalt, which reddens litmus paper, and is almost wholly soluble in water.

40. Sesquichloride of arsenic. Described in Vol. I. p. 306.

Muriatic acid dissolves a little arsenic. The solution is colourless, has a very acid taste, and when diluted with water most of the arsenic is deposited in the state of arsenious acid.

- 41. Chlorides of antimony. Described in Vol. I. p. 322.
- 42. Chloride of chromium. See Vol. I. p. 337.
- 43. Chloride of uranium. Not yet investigated.

The solution of uranium in muriatic acid has a yellowish green colour. When it is mixed with ether and exposed to the direct rays of the sun green flocks precipitate, which are considered as muriate of uranium. They dissolve in water with a dark green colour. Protoxide of uranium dissolves in muriatic acid with a bottle green colour.

Peroxide of uranium dissolved in muriatic acid has a yellowish green colour. According to Lecanu, the acid may be saturated with this peroxide, and when sufficiently concentrated deposites needles, which are exceedingly deliquescent.

- 44. Chlorides of molybdenum. Described in Vol. I. p. 357. The solutions of the chlorides in water present so little difference from the anhydrous chlorides that a particular detail seems unnecessary.
  - 45. Chlorides of tungsten. Described in Vol. I. p. 367.

Tungsten is somewhat soluble in concentrated muriatic acid. When the solution is diluted a caseous white matter falls, which is considered as a subsalt.

- 46. Terchloride of columbium. Described in Vol. I. p. 375. Columbic acid dissolves in muriatic acid and the solution is not precipitated by dilution with water.
  - 47. Bichloride of titanium. Described in Vol. I. p. 385.

Hydrated titanic acid dissolves by boiling in muriatic acid, and constitutes a yellow coloured solution, which by cautious evaporation may be freed from its excess of acid. When evaporated to dryness, and redissolved in water, a residue of titanic acid remains, no longer soluble in muriatic acid.

#### SECTION II. -- OF CHLORO-STANNATES.

Both of the chlorides of tin possess the characters of an acid, and are capable of combining with chlorine bases, though only a very few of these salts have been hitherto investigated. The following are well known.

1. Chloro-stannate of ammonia. This salt may be obtained by dissolving chloride of tin and sal ammoniac in atomic proportions, and concentrating the solution. It crystallizes in oblique prisms with angles of about 55° and 125°, terminated by a dihedral summit, the faces of which replace the angles at the base of the obtuse edges of the prism. The crystals are white with a shade of yellow, and opaque with the diamond lustre, which characterizes nitrate of lead. The crystals are not altered by exposure to the air, have the characteristic taste of salts of tin, are soluble in water, and seem to contain a little water. The constituents, as determined by Dr. Apjohn, are

1 aton	n chloride of	tin	•	•	12.75
1 aton	n sal <mark>-ammo</mark> n	iac	•	•	6.75
1 aton	a water	•	•	•	1.125
					20.625*

2. Bichloro-stannate of tin. This salt is easily obtained by dissolving fuming liquor of Libavius and sal ammoniac in water in the atomic proportions, and concentrating the solution. The salt crystallizes in transparent octahedrons, usually elongated in one direction. The first crystals of this salt that I saw I received from Dr. Apjohn of Dublin. It is soluble in water, has the characteristic taste of the salts of tin, and seems to be anhydrous. Its constituents, as determined by Dr. Apjohn, are

1	atom	bichloride of tin	•	•	17.25
1	atom	sal-ammoniac	•	•	6.75
					24+

3. Chloro-stannate of potash. This salt is easily obtained by dissolving chloride of tin and chloride of potassium in water in the atomic proportions and concentrating the solution. The salt crystallizes in four-sided prisms, deviating only a few degrees from being rectangular. These crystals are opaque, have a

shade of yellow and the diamond lustre, which characterizes chloro-stannate of ammonia. They are soluble in water, and have the characteristic taste of salts of tin. They are anhydrous. I have not subjected them to analysis, but consider them as composed of

- 4. Chloro-stannate of sodium. Crystallizes, according to Berzelius, in fine needles.
- 5. Chloro-stannate of barium. Crystallizes in oblique four-sided prisms.

Several other salts belonging to this species have been formed, but as they have not been particularly examined, I think it needless to give a list of them here.

## SECTION III. -- OF CHLORO-HYDRARGYRATES.

Bonsdorf has shown that corrosive sublimate possesses the characters of an acid, and that it is capable of combining with other chlorides, and forming a class of salts to which he has given the name of chloro-hydrargyrates. The following are the salts of this nature with which we are at present acquainted.

- 1. Bichloro-hydrargyrate of sal ammoniac. This salt was known to the alchymists, and much celebrated for its virtues under the names of sal alembroth, salt of wisdom, salt of art, &c. It is easily obtained by mixing together sal ammoniac and corrosive sublimate, and dissolving them in water. Sal ammoniac was observed to have the property of increasing the solubility of corrosive sublimate prodigiously. One part of sal ammoniac dissolved in 3 parts of water, will enable the liquid to take up no less than 5 parts of corrosive sublimate. When we mix these substances in the proportion of 2 atoms corrosive sublimate, 1 atom of sal ammoniac, and 8 atoms of water, the mixture is liquid at the temperature of 140°: on cooling, it concretes into a needle-form mass. From the experiments of Dr. John Davy, it would appear that the following mixtures also form chemical compounds.
- 1. 2 atoms corrosive sublimate, 1 atom sal ammoniac, and 16 atoms water; liquid at 85°, and solid at 55°. The specific gravity in the liquid form is 1.98.
- 2. 2 atoms corros. sub., 1 sal amm., 32 water; is liquid at 55°, and has a specific gravity of 1.58.

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3. 2 atoms corros. sub., 1 sal amm.,  $10\frac{2}{3}$  water; is liquid at about  $105^{\circ}$ ; on cooling slowly to  $60^{\circ}$ , it deposites crystals which consist of four-sided flat prisms.\*

From these observations of Dr. Davy, and many others of a similar nature made by others, it would appear that this salt is a compound of

2 atoms chloride of mercury	•	34
1 atom sal ammoniac .	•	6.75
•		40.75

The water varies in its quantity, probably from 4 atoms to 8, constituting 4 different species of this salt.

- 2. Chloro-hydrargyrate of potassium. Of this salt there are three species, which have been examined, described, and analyzed by M. Bonsdorf.
- (1.) Quater-chloro-hydrargyrate of potassium. When a saturated solution of chloride of potassium is mixed cold with corrosive sublimate in powder, an abundant solution is effected; but in a short time needles are deposited, and the solution stops short. However, if we heat to 122°, the solution becomes capable of dissolving an additional quantity of corrosive sublimate. On cooling, it becomes almost wholly a mass of asbestiform needles, having a silky lustre. It is very soluble in hot water. A saturated solution at 64°.5, deposites a prodigious number of crystals when cooled down to 60°. When cooled very slowly, the crystals are right rhombic prisms, with angles of 112° and 78°. The constituents of this salt, as determined by the analysis of Bonsdorf, are

4 atoms chloride	of merci	ury	•	68
1 atom chloride o	of potass	ium	•	9.5
4 atoms water	•	•	•	4.5
				80.01

(2.) Bichloro-hydrargyrate of potassium. When a cold solution of chloride of potassium is saturated as above described with corrosive sublimate, if we heat it to 86°, and after adding a few drops of water, saturate it with as much additional corrosive sublimate as it will take up by agitation, and then after filtration allow it to cool in the ordinary temperature of the air, the first crystals deposited are usually of the asbestiform kind. The clear liquid being now poured into a new vessel,

<sup>\*</sup> Phil. Trans. 1822, p. 362. † Ann. de Chim. et de Phys. xliv. 194.

and left to spontaneous evaporation, needle-form' crystals in sect. III. stars are deposited. These crystals constitute the salt in question, being, according to Bonsdorf's analysis, composed of

2 atoms chloride		•	$\hat{34}$		
1 atom chloride o	of pot	assiun	ı	•	9.5
2 atoms water			•	•	2.25
					45.75*

(3.) Chloro-hydrargyrate of potassium. When a cold solution of chloride of potassium is saturated with chloride of mercury, if we add an equal quantity of chloride of potassium to that already present, and leave the liquid to spontaneous crystallization, large crystals are gradually deposited, usually in right rhombic prisms, the faces of which meet at an angle of 110°. These crystals have a very slight tinge of yellowish gray. They are not altered by exposure to the atmosphere. constituents of this salt, as determined by Bonsdorf, are

1 atom	chloride	e of m	ercury	y	•	17
1 atom	chloride	e of po	otassiu	ım	•	9.5
1 atom	water	•	•	•	•	1.125
						<del></del>
						05 00 5

27.625+

3. Bichloro-hydrargyrate of sodium. When corrosive sublimate is dissolved in a cold saturated solution of common salt till the liquid refuses to dissolve any more, and the solution abandoned to spontaneous crystallization, we obtain a mass of crystals in needles, composed of the two constituents. These crystals are irregular six-sided prisms. They are soluble in water, and not altered by exposure to the air. According to the analysis of Bonsdorf, they are composed of

2 atoms chloride of	merc	eury	•	34
1 atom chloride of	sodiu	m	•	7.5
4 atoms of water	•	•	•	4.5
				16+
				46†

4. Chloro-hydrargyrate of lithium. The chloride of lithium dissolves corrosive sublimate readily, and when the solution is concentrated, deposites crystals in needles. One portion of this compound is deliquescent, while another portion remains unaltered. Hence it is probable that there are two species of this salt.8

<sup>\*</sup> Ann. de Chim. et de Phys. xliv. 196. + Ibid. ‡ Ibid. p. 199.

<sup>§</sup> Bonsdorf, ibid. p. 201.

5. Sesqui-chloro-hydrargyrate of barium. Cold saturated solution of chloride of barium, when saturated with corrosive sublimate, and left to spontaneous evaporation, deposites first crystals of chloride of mercury, then needles and plates resembling prehnite, and, lastly, tabular crystals, either isolated or in bundles. They consist of oblique rhombic prisms, whose faces meet at angles of 85° and 95°. All of these crystals have the same composition, being composed, according to Bonsdorf's analysis, of

$\mathbf{C}$	hloride	of	merc	eury	•	•	•	•	$65 \cdot 235$
	hloride					•		•	29.080
V	<b>Vater</b>		•	•	•	•	•	•	7.685
mu.	1								102.000*
This ap	pproaci atoms		lorid	a of	mara	11 117			25
1 2							•	•	
1	atom			or	oariur	n	•	•	. 13
3	atoms	wa	iter				•	•	3.375
									41.375

- 6. Chloro-hydrargyrate of strontium. May be formed in the same way as the preceding salts. It is very soluble, and crystallizes in needles, not altered by exposure to the air.+
- 7. Quinto-chloro-hydrargyrate of calcium. When a cold saturated solution of chloride of calcium is mixed with corrosive sublimate, we obtain an oily looking liquid, which by evaporation yields two different species of salt.

When evaporated in a gentle and uniform heat, or in the vacuum of an air-pump, over sulphuric acid, the crystals deposited are regular octahedrons or tetrahedrons. These crystals are transparent and very brilliant, and are not altered by exposure to the air. When sprinkled with water they become white and are not decomposed. Water dissolves the chloride of mercury, and leaves the chloride of calcium. The constituents of this salt, according to the analysis of Bonsdorf, are

5 atoms chloride of mercury	•		85
l atom chloride of calcium		•	8
8 atoms water	•	•	9
			102t

<sup>\*</sup> Bonsdorf, Ann. de Chim. et de Phys. xliv. 201.

<sup>†</sup> Ibid. p. 202. ‡ Ibid.

Sect. III.

When the solution after the deposition of the octahedral crystals is cooled, it deposites needle-form crystals in abundance, and when cooled down below 32° it becomes almost solid. When heated, the salt redissolves, and if the liquid be kept in the temperature of 86°, it deposites large crystals, consisting sometimes of six-sided prisms, and sometimes of rhomboidal tables, with angles of about 110°. These crystals are very soluble in water, and so deliquescent that it is difficult to preserve them solid. In the vacuum of an air-pump over sulphuric acid, they lose their water of crystallization and effloresce. Bonsdorf did not succeed in determining the quantity of water in this salt; but the other constituents are

2 atoms chloride of mercury	•	٠.	34
1 atom chloride of calcium	•	•	8
			49*

It is therefore a bichloro-hydrargyrate of calcium

8. Terchloro-hydrargyrate of magnesium. This salt is obtained by the same process as the preceding. When concentrated by a gentle heat, and then cooled slowly, large crystalline plates are deposited, united in the form of a cross. These crystals are permanent in the air whether moist or dry. They are rhomboidal prisms, when struck they break into several oblique rhomboids, as is the case with gypsum. Sometimes this salt crystallizes nearly in the form of Glauber salt. It is soluble in alcohol, as well as water, and crystallizes very well by evaporation. Its constituents, according to Bonsdorf's analysis, are

3 atoms chloride of mercury	•	•	51
1 atom chloride of magnesium	•	•	7
5 atoms water	•	-	5.625
	_		63.625+

9. Chloro-hydrargyrate of magnesium. If we decant off the mother liquor after the deposition of the crystals of the preceding salt, and put it under the exhausted receiver of the airpump, over sulphuric acid, it deposites fine crystals, consisting of flat rhombic prisms. These crystals are exceedingly deliquescent. Their constituents, according to Bonsdorf, are

<sup>\*</sup> Bonsdorf, Ann. de Chim. et de Phys. xliv. 203.

1 atom chloride of mercury	•	•	17
1 atom chloride of magnesium	•	•	7
6 atoms water	•	•	6.75
,			30.75*

- 10. Chloro-hydrargyrate of glucinum. This salt crystallizes in right rhombic prisms.†
- 11. Chloro-hydrargyrate of yttrium. It forms cubic crystals which appear to be deliquescent.
- 12. Chloro-hydrargyrate of cerium. It crystallizes in cubes, not altered by exposure to the air.§
- 13. Chloro-hydrargyrate of iron. When the crystallized green chloride of iron is dissolved in water, the liquid takes up a great deal of chloride of mercury; but allows a portion of it to fall during evaporation, as is the case with some other similar solutions. When the mother water is evaporated in the exhausted receiver of an air-pump over sulphuric acid, it deposites beautiful crystals in rhombic prisms; which sometimes from truncation of the edges have 6, 8, or 10 faces. The colour is honey yellow. When exposed to the air (unless it be very dry) they deliquesce and undergo slow decomposition, depositing a brownish yellow powder. It seems to be a compound of

1 atom chloride of mercury	•	•	17
1 atom chloride of iron		•	· 8
4 atoms water	•	•	4.5
			29.5

14. Chloro-hydrargyrate of manganese. When this solution is formed like the preceding, it deposites crystals of chloride of mercury. The mother water being exposed to a new evaporation, deposites transparent crystals, having a red colour, and precisely the form of the chloro-hydrargyrate of iron. They deliquesce in moist air, or when handled. In the vacuum of a receiver, over sulphuric acid, they effloresce. This salt, according to the analysis of Bonsdorf, is composed of

1 atom chloride of mercury	•	•	17
1 atom chloride of manganese	•	•	8
4 atoms water	•	•	4.5

<sup>\*</sup> Bonsdorf, Ann. de Chim. et de Phys. xliv. p. 205. † Ibid. p. 206.

29·5¶

<sup>‡</sup> Ibid. § Ibid. p. 244. ¶ Ibid. p. 246. ¶ Ibid. p. 244.

15. Chloro-hydrargyrate of nickel. The solution made in same way as the preceding deposites by spontaneous evaporation regular tetrahedrons, having an apple green colour. These crystals are not altered by exposure to the air. This salt has not been analyzed, but its constituents are probably in the same proportions as the quinto-chloro-hydrargyrate of calcium, which crystallizes in the same shape.

When the mother water is put into the vacuum of an airpump, over sulphuric acid, it deposites new crystals, some of, which are long prisms, others, short and very oblique prisms, whose obtuse angle is about 130°. These crystals deliquesce unless the air be dry.\*

- 16. Chloro-hydrargyrate of cobalt. This salt crystallizes in beautiful prisms of a bluish red colour. They are isomorphous with the crystals of the chloro-hydrargyrate of iron and man-ganese. They deliquesce unless the air be dry.+
- 17. Chloro-hydrargyrate of zinc. A solution of chloride of zinc saturated with chloride of mercury, when left to spontaneous evaporation, deposites fine rhombic prisms of chloride of mercury. The mother water crystallizes with difficulty even over sulphuric acid. It deposites prismatic needles and tables, which are very deliquescent.‡
- 18. Chloro-hydrargyrate of copper. It crystallizes in prismatic needles, and is not altered by exposure to the air.§
  19. Chloro-hydrargyrate of lead. This salt cannot be formed on account of the little solubility of chloride of lead.

# SECTION IV. --- OF CHLORO-AURATES.

Several of these salts have been known for a considerable time; but it is only of late, and in consequence of the investigations of Bonsdorf, that we have become acquainted with their nature.

1. Bichloro-aurate of potassium. This salt may be obtained by mixing together solutions of chloride of gold and chloride of potassium, and concentrating the solution till it deposites The shape of the crystal is a four-sided prism; its colour is yellow. When exposed to the air it slightly effloresces. When heated it gives out water, and then melts into a dark red liquid, which, when kept in a high red heat, slowly gives out chlorine, and leaves a mixture of gold and chloride

<sup>\*</sup> Bonsdorf, Ann. de Chim. et de Phys. xliv. p. 244.

<sup>†</sup> Ibid. p. 244. † Ibid. p. 245. § Ibid. p. 246.

of potassium. The salt is very soluble in water, and the solution has a yellow colour. It is very acrid, and like all the soluble salts of gold, acts as a poison. The constituents of this salt, according to the analysis of Javal, are

2 atoms sesquichloride of gold	•	•	$38 \cdot 5$
1 atom chloride of potassium	•	•	$9 \cdot 5$
3 atoms water	•	•	3.375

51.375\*

2. Chloro-aurate of sodium. This salt is easily formed by evaporating to dryness a solution of 4 parts of gold in aqua regia, dissolving the residue in 8 parts of water, adding 1 part of common salt, and then concentrating the solution, and allowing it to cool. Long orange yellow four-sided prisms are deposited, constituting the chloro-aurate. These crystals are not altered by exposure to the air. When heated they give out water, and then melt, and in a red heat give out chlorine; but it requires a very long continued application of heat to drive off the whole of the chlorine. This salt, according to the analysis of Figuier, is composed of

2 atoms sesquichloride of gold	•	•	38.5
1 atom chloride of sodium	•	•	7.5
6 atoms water	•	•	6.75
			59.75.

52.75+

In my experiments on gold, I obtained another chloro-aurate of sodium, composed of

2 atoms chloride of gold	l .	34
1 atom chloride of sodiu	m	7.5
8 atoms water .	•	9
		50.5

90.9

Probably the same chloro-aurate of potassium also exists.

- 3. Chloro-aurate of barium. This salt has a brown colour, and crystallizes in short rhombic prisms, the obtuse edges of which constitute angles of 105°. In dry air it remains unaltered; but it deliquesces in a moist atmosphere.
- 4. Chloro-aurate of strontium. Yellow. It crystallizes in rhombic prisms permanent in the air.§

<sup>\*</sup> Ann. de Chim. et de Phys. xvii. 337.

<sup>†</sup> Jour. de Phasmie, vi. 64, and viii. 157.

<sup>‡</sup> Bonsdorf, Ann. de Chim. et de Phys. xliv, 256.

<sup>§</sup> Ibid.

5. Terchloro-aurate of calcium. It usually constitutes acicular crystals consisting of rhombic prisms. They are not altered by dry air; but deliquesce when the atmosphere is moist. By the analysis of Bonsdorf, the salt is composed of

6 atoms water . . . . . 6.75

71.5\*

6. Terchloro-aurate of magnesium. When concentrated in the vacuum of an air-pump over sulphuric acid it crystallizes in short-rhomboidal prisms with edges of 72° and 108°. The colour is a fine yellow. In dry air it remains unaltered but deliquesces in moist air. In a gentle heat it loses its water of crystallization, and melts into a deep brown liquid which exhales chlorine, and at last it dries. Its constituents, according to the analysis of Bonsdorf, are

3 atoms sesquich	•	•	57.75			
1 atom chloride	•	•	6			
12 atoms water	•	•	•	•	•	13.5
						77:25+

- 7. Chloro-aurate of manganese. Crystallizes in yellow rhomboidal prisms, which deliquesce in moist air. It is probably isomorphous with the two preceding salts.‡
- 8. Chloro-aurate of nickel. Crystallizes in short rhomboidal prisms, colour greenish-yellow, isomorphous with the terchloro-aurate of manganese.
- 9. Chloro-aurate of cobalt. Crystals very oblique rhombic prisms, of a deep yellow, and not altered by exposure to the air. ||
- 10. Chloro-aurate of zinc. Similar in appearance to the chloro-aurate of magnesium, to which it is isomorphous. Permanent in a dry atmosphere.
- 11. Chloro-aurate of cadmium. Its colour is deeper than that of the preceding salt. It crystallizes in prismatic needles permanent in the air. \*\*

#### SECTION V.-OF CHLORO-PLATINATES.

For the investigation of most of the species belonging to

\* Bonsdorf, Ann. de Chim. et de Phys. xliv. p. 257. † Ibid. p. 258. § Ibid. p. 259. || Ibid. p. 258. ¶ Ibid. \*\* Ibid.

Class II. th

this class of salts, with which we are at present acquainted, we are indebted to the industry of M. Bonsdorf.

1. Chloro-platinate of ammonia. When a solution of sal ammoniac is added to liquid chloride of platinum a beautiful orange-yellow precipitate falls, consisting of very small octahedrons. It is tasteless. Very little soluble in water. When heated, sal ammoniac and chlorine are disengaged, and metallic platinum remains. It is a compound of

1 atom bichloride of platinum	•	•	21
1 atom sal ammoniac	•	•	6.75
			27.75

2. Chloro-platinate of potassium. This salt was obtained by Magnus by dissolving chloride of platinum in a minimum of muriatic acid, adding chloride of potassium in the requisite proportions, and evaporating. Red prisms are obtained easily soluble in water; but insoluble in alcohol; which throws down the salt in needles from the aqueous solution. This salt, like the preceding, is anhydrous, and composed, according to Magnus, of

	•		26.0
	, ,		
1 atom chloride of potassium	•	•	9.5
I atom chloride of platinum	•	•	16.5

3. Bichloro-platinate of potassium. This is the common yellow precipitate which falls when a salt of potash is added to an aqueous solution of chloride of platinum. It consists of very small octahedrons, very little soluble in water, and not at all in alcohol. When heated it gives out chlorine and leaves a mixture of platinum and chloride of potassium. Its constituents, according to the analysis of Berzelius, are

1 atom bichloride of platinum 1 atom chloride of potassium	•	•	21 9·5
			00 -

4. Chloro-platinate of sodium. This salt is formed when common salt is added to a solution of chloride of platinum, and the mixture is sufficiently concentrated. The liquid deposites beautiful orange-red prisms or triangular tables. When heated it falls down into a yellow coloured powder, and by a stronger heat chlorine is driven off, and there remains a mix-

<sup>\*</sup> Poggendorf's Annalen, xiv. 241.

ture of platinum and chloride of sodium. The constituents of this salt, as determined by the analysis of Berzelius, are

5. Chloro-platinate of barium. When a mixture of chloride of platinum and chloride of barium in slight excess is left to spontaneous evaporation, we obtain yellow prisms, which are easily separated from the excess of chloride of barium by a little water, which dissolves them without touching the chloride of barium. By a second crystallization they are obtained quite pure. The crystals, when pure, are deep orange, similar both in shape and colour to the natural chromate of lead, or oblique prisms with angles of about 107° and 73°. These crystals are not altered by exposure to the air. When heated to the temperature of 158° they effloresce and fall into powder. But a higher temperature is necessary to make them lose all their water of crystallization. The constituents of this salt, according to the analysis of Bonsdorf, are

6. Chloro-platinate of strontium. It is prepared in the same way as the preceding salt. It is very soluble in water, and crystallizes in rhombic prisms, one of the angles of which is about 93°; but in general we obtain it only in a fibrous or compact mass. It is not altered by exposure to the air; but effloresces when heated. Its constituents, by Bonsdorf's analysis, are

1 atom blenioria		4			•	21
1 atom chloride	of st	rontiu	m	•	•	10
8 atoms water	•		•	•	•	9
						40+

7. Chloro-platinate of calcium. When solutions of the two constituents of this salt are mixed and left to spontaneous evaporation sometimes crystals in dendrites are formed like sal ammoniac, sometimes a yellow coloured transparent gelatinous

† Ibid. p. 249.

<sup>\*</sup> Poggendorf's Annalen, xiv. p. 248.

mass. To obtain regular crystals we should add an excess of chloride of calcium. Bonsdorf obtained it on one occasion in small rhombic prisms. A gentle heat drives off the water of crystallization, and changes it into a dull looking powder; but on exposure to the air it again imbibes the water driven off. Its constituents, as determined by Bonsdorf, are

1 atom bichlori	•	•	21			
1 atom chloride	of c	alcium		•	•	7
8 atoms water	•	•	•	•	•	9
•						37*

8. Chloro-platinate of magnesium. Obtained by mixing solutions of the constituents, and abandoning them to spontaneous crystallization. The crystals are sometimes rhomboids, with faces whose greater angles are about 130°. They are often in small needles, or radiated bundles, having a silky lustre. This salt has a golden-yellow colour; is not altered by exposure to the air; is very soluble in water. When heated, it loses its water of crystallization, and falls into a yellowish brown dirty powder. When left exposed to the air, it recovers exactly the quantity of water which it had lost, forming a coherent mass with the original yellow colour. The constituents of this salt, as determined by the analysis of Bonsdorf, are

1 atom bichloride	•	21			
1 atom chloride o	of mag	gnesiu	m	•	6
6 atoms water	•	•	•	•	6.75
					33.75+

9. Chloro-platinate of iron. The salt is best obtained by evaporating the mixture of the two constituents under the exhausted receiver of an air-pump over sulphuric acid. It has a deep brown colour, and has the same crystalline shape and constitution as the preceding salt; namely,

1 atom bichloride of platinum					21
1 atom chloride of iron				•	8
6 atoms water	toms water	•	•	•	6.75
					<del></del>
v				•	35·75±

10. Chloro-platinate of manganese. Similar to chloro-platinate of magnesium, excepting that it has a deeper brown colour.

<sup>\*</sup> Poggendorf's Annalen, xiv. p. 250. † Ibid. p. 251. ‡ Ibid. p. 253.

Its constituents are the same as those of the other isomorphous \_sect. vi. salts just described; namely,

•	1 atom bichlorid	•	21			
	1 atom chloride	of mai	ngane	se	•	8
	6 atoms water	•	•	•	•	6.75
	-					
						35.75*

- 11. Chloro-platinate of cobalt. Similar to the preceding in all respects, even in colour.
- 12. Chloro-platinate of nichel. Its colour is greenish yellow, but in every other respect it is similar to the preceding salt, even its constituents are the same as those of chloro-platinate of manganese.‡
- 13. Chloro-platinate of zinc. When concentrated solutions of the constituents of this salt are mixed, they deposite a yellow salt in needles. On adding a little water, the crystals redissolve, but are again produced by evaporation. Lustre silky, colour a fine golden yellow, not altered by exposure to the air.§
- 14. Chloro-platinate of cadmium. This salt is similar to the preceding; but its colour approaches that of chloro-platinate of manganese.
- 15. Chloro-platinate of copper. Similar to chloro-platinate of nickel, excepting that its colour is a deeper green. It deliquesces in moist air. It is best crystallized in the vacuum of an air-pump over sulphuric acid; but it effloresces if it be left too long. Bonsdorf obtained it in beautiful prisms, terminated by a rhomboidal face; but in general it crystallizes in needles. Its constituents, according to the analysis of Bonsdorf, are

1 atom bichloride	e of pl	atinu	m	•	<b>25</b>
1 atom chloride	of cop	per	•	•	8.5
6 atoms water	•	•	•	•	6.75

40·25¶

This is the constitution also of the eight preceding salts, which are all isomorphous.

## SECTION VI. -- OF CHLORO-PALLADIATES.

The chloride of palladium combines with chloride bases, when, after adding a little muriatic acid, the solutions are

*	Poggendorf's Annalen, xiv. 253.	† Ibid. p. 255.	‡ Ibid.
Ş	Ibid. p. 254.	Ibid. p. 255.	'¶ Ibid.

mixed together. The mixture must be evaporated to dryness, and the residue dissolved in water, and crystallized in the vacuum of an air-pump over sulphuric acid. The chloro-palladiates hitherto examined are very soluble in water, and soluble also in alcohol. They have usually a brown colour.

1. Dichloro-palladiate of ammonia. When ammonia in excess is added to a solution of chloride of palladium, the yellow precipitate which falls at first is redissolved. By evaporating to dryness, and digesting the residue in water, a yellowish green insoluble powder remains. Its constituents are

l atom chlorine		•	•	4.5
1 atom palladium	•	•	•	6.75
l atom ammonia	•	•	•	2.125

2. Chloro-palladiate of potassium. Described in vol. i. p. 677. It is composed of

1 atom bichloride of palladium	•	15.75
1 atom chloride of potassium	•	9.5
		25.25

- 3. Chloro-palladiate of sodium. A red coloured salt, fusible, soluble in alcohol.
- 4. Chloro-palladiate of barium. It crystallizes in dendrites, which vegetate on the edges of the glass, and are not altered by exposure to the air.\*
- 5. Chloro-palladiate of calcium. It forms prismatic crystals of a light brown colour, and deliquescing in the air.+
- 6. Chloro-palladiate of magnesium. Forms prismatic needles, permanent in dry, but deliquescing in moist air.‡
- 7. Chloro-palladiate of manganese. It crystallizes in cubes or in rhomboids, differing but little from cubes. Colour so deep a brown, that it appears black by reflected light. Not altered by exposure to the air.§
- 8. Chloro-palladiate of nickel. Rhomboids, or rhomboidal prisms, of a deep brownish green. The lateral angles deviate very little from 90°. Not altered by exposure to the air.
- 9. Chloro-palladiate of zinc. Needle-form crystals in diverging rays. Colour brown. Deliquesces rapidly when exposed to the air.¶

<sup>\*</sup> Bonsdorf, Ann. de Chim. et de Phys. xliv. 259. † Ibid. † Ibid. § Ibid. | Ibid. p. 260. ¶ Ibid.

10. Chloro-palladiate of cadmium. Fine needles of a fine Sect. VIII. brown colour. It does not deliquesce when exposed to the air.\*

# SECTION VII. -- OF CHLORO-RHODIATES.

This genus of salts, owing to the difficulty of procuring rhodium in sufficient quantity, has been very little investigated.

1. Chloro-rhodiate of potassium. When finely pulverized rhodium is mixed with chloride of potassium, and ignited in a glass tube, while a current of chlorine gas is passed through it, the whole is converted into a red coloured mass. Dissolve this mass in water, and precipitate the chloro-rhodiate by alcohol. Wash the red precipitate with alcohol of 0.840, till the excess of chloride of potassium is removed. The chloro-rhodiate thus obtained is a red powder, which may be crystallized by solution in water, and the proper degree of concentration. Its constituents, according to the analysis of Berzelius, are

1 atom sesquichlo	•	11.5			
1 atom chloride o	•		9.5		
4 atoms water	- •	•	•	•	4.5
			•		25.5

2. Chloro-rhodiate of sodium. This salt may be obtained by the same process as the preceding, merely substituting common salt for chloride of potassium. It was obtained originally by Dr. Wollaston, by the process described in vol. i. p. 680. The constituents of this salt are

1 atom sesquichlori	•	1 l·5			
1 atom common sal	lt .	•	•	•	7.5
9 atoms water .	•	•	•	•	10.125
					29.125

#### SECTION VIII. -- OF CHLORO-IRIDIATES.

This genus of salts is still as little explored as the preceding, and for the same reason—the great scarcity of iridium.

1. Chloro-iridiate of potassium. This salt has been described in vol. i. p. 690. Its constituents, according to the analysis of Berzelius, are

1 atom sesquichloride of iridium	•	19
1 atom chloride of potassium	•	9.5
		28.5

<sup>\*</sup> Bonsdorf, Ann. de Chim. et deePhys. xliv. 260.

2. Bichlaro-iridiate of potassium. The method employed by Berzelius for forming this salt was the following. Through an intimate mixture of iridium and chloride of potassium, raised to a low red heat, a current of chlorine gas is passed. matter is now dissolved in water, to separate the iridium still remaining in the metallic state, and the filtered solution being mixed with a little aqua regia, is evaporated to dryness. The excess of chloride of potassium is removed by washing the residue with a little cold water. It is now dissolved in boiling water, and a little aqua regia being added, the salt is crystal-This salt dissolves easily in pure water with a deep red colour; but in water saturated with chloride of potassium, it is not soluble; neither is it soluble in alcohol. In a low red heat it is not altered; but a strong red heat deprives it of chlorine, and converts it into the preceding salt. Its constituents, as determined by Berzelius, are

1 atom bichloride of iridium . 21·25
1 atom chloride of potassium . 9·5
30·75

3. Terchloro-iridiate of potassium. When the grains composed of osmium and iridium, after being heated to redness with saltpetre, are digested in water, both the aqueous solution and the undissolved powder being distilled with aqua regia and the liquid remaining in the retort being filtered, mixed with chloride of potassium, and evaporated to dryness, a dark red matter remains. Wash this matter with a little water, which will dissolve little but chloride of potassium. Dissolve the remaining dark red matter in water, evaporate to dryness, wash the residue with alcohol of 0.840, and then dissolve it in water, and leave the solution to spontaneous crystallization.

The crystals are oblique prisms with rhomboidal bases. By reflected light they appear brown, by transmitted light ruby red. This salt, according to the analysis of Berzelius, is composed of

1 atom terchloride of iridium . 25.75
1 atom chloride of potassium . 7.5
33.25\*

4. Sesquichloro-iridiate of sodium. When the sesquichloride of iridium is mixed with common salt and evaporated it is not

<sup>\*</sup> A description of the mode of obtaining this salt is given in Vol. I. p. 691.

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decomposed as when chloride of potassium is used, but gives a coal black compound, fusible by heat, and deliquescing when expessed to the air. It dissolves readily in water and in alcohol, and the solution has a blood red colour.\*

5. Bichloro-iridiate of sodium. Obtained by a process similar to that by which the bichloro-iridiate of potassium is formed. It crystallizes in black tables and in four-sided prisms, and is isomorphous with the corresponding platinum salt.†

# SECTION IX. OF CHLORO-OSMIATES.

- 1. Chloro-osmiate of ammonia. This salt was obtained by Berzelius by passing a current of chlorine gas over osmium heated in a glass tube, and allowing the vapour to pass into an aqueous solution of ammonia. Evaporate to get rid of the excess of ammonia. Apply a moderate heat to the brown coloured residue to drive off the excess of sal ammoniac, a greenish residue remains which is the salt in question.
- 2. Sesquichloro-osmiate of ammonia. Dissolve the ammonia-sesquioxide of osmium in muriatic acid, and evaporate the dark yellowish brown solution to dryness. The salt remains in the form of a black uncrystallizable mass, not altered by exposure to the air. When heated it becomes imperfectly liquid, and then undergoes decomposition. It is soluble in water.‡
- 3. Terchloro-osmiate of ammonia. A current of chlorine gas passed over osmiate of iridium was received in weak ammonia till the alkali was saturated. This liquid after some days was placed in contact with an excess of muriatic acid and with mercury. The brownish purple liquid in 48 hours lost all smell of osmium. It was evaporated to dryness, and the dry residue was digested with alcohol. The alcoholic solution had a beautiful red colour. Being left to spontaneous evaporation it deposited the terchloro-osmiate in the state of a brown confused crystalline mass. It is soluble in water. When heated it gives off sal ammoniac.§
- 4. Chloro-osmiate of potassium. It may be obtained by mixing the two constituents and evaporating the mixture. It crystallizes in prisms having a brown colour. Alcohol being added, a great deal of the osmium is reduced to the metallic state. This salt is much more soluble in water than in alcohol.
- 5. Bichloro-osmiate of potassium. Equal weights of osmium and chloride of potassium are exposed at a red heat in a glass

Class III. tube to a stream of chlorine gas. From the dark red powder formed by this process the excess of chloride of potassium is washed out by a little water, the residue is now dissolved in water and allowed to crystallize spontaneously. The crystals are regular octahedrons of a dark brown colour, and having considerable lustre. The powder is cinnabar red. The constituents of this salt, according to the analysis of Berzelius, are

1 atom bichloride of osmium 1 atom chloride of potassium 9.531.0

# CLASS III.

#### BROMINE ACID SALTS.

The analogy between chlorine and bromine is so perfect, that we cannot have the least doubt that both are capable of entering into similar combinations. But from the short time that bromine has been known it is evident, that many of its combinations must still be unexamined. Indeed the only salts of bromine with which we are at present acquainted, are the hydrobromates or bromides.

### SECTION I.—OF THE BROMIDES OR HYDROBROMATES.

These salts are easily recognised by the property which they have of becoming yellow and giving out bromine when they are acted on by bodies which have a strong affinity for hydrogen, as chloric acid, nitric acid, and especially chlorine. the bromides are decomposed by chlorine with the disengagement of bromine.

1. Hydrobromate of ammonia. Hydrobromic acid gas and ammoniacal gas unite when mixed in equal volumes, and condense into a salt. It is solid and white; when exposed to the action of the air it becomes slightly yellow, and acquires the property of reddening litmus paper. It crystallizes in long prisms. Heat volatilizes it.\* From the phenomena of its formation it is obvious that it is a compound of

<sup>\*</sup> Balard, Ann. de Chim. et de Phys. xxxii. 358.

1 atom hydrobromic acid	•	•	10.125	Sect. I
l atom ammonia .	•	•	<b>2·125</b>	***************************************

12.25

2. Bromide of potassium. Described in Vol. I. p. 403.

3. Bromide of sodium. Aqueous hydrobromic acid dissolves soda, and when the solution is concentrated it deposites crystals containing water of crystallization. In a red heat they melt, give out their water, and bromide of sodium remains, composed of

4. Bromide of barium. This salt may be formed by agitating the ethereal solution of bromine with hydrated barytes, or by dissolving barytes in hydrobromic acid. It is very soluble in water, and the crystals are opaque tubercles grouped together, and quite unlike the crystals of chloride of barium. The taste is similar to that of chloride of barium, but harsher. It is soluble in alcohol.\* A current of carbonic acid gas passed through it gives it a yellow colour. Its constituents, according to the analysis of 4,0 wig, are

1. atom bromine	•	•	•	10
1 atom barium	•	•	•	8.5
l atom water	•	•	•	1.125
				19:625

5. Bromide of strontium. Still unknown.

6. Bromide of calcium. It may be obtained by passing vapour of bromine over red hot lime. A white matter having a sharp and bitter taste, deliquescing in the air, and soluble in water, with the evolution of heat. The aqueous solution crystallizes with difficulty, and the crystals contain much water. The anhydrous bromide is composed, according to Löwig, of

1 atom bromine	•	•	•	10
1 atom calcium	•	•	•	2.5
				12.5

<sup>\*</sup> Balard, Ann. de Chim. et de Phys. xxxii. 358.

<sup>†</sup> I have not seen Löwig's paper, which seems to have been a Thesis, published at Heidelberg in 1829, but take the observations of Löwig from L. Gmelin's Handbuch, vol. ii. 1579, &c.

- 7. Bromide of magnesium. Bromine does not decompose ignited magnesia, but the decomposition takes place if the magnesia be intimately mixed with charcoal.\* The bromide dissolves in water and forms a deliquescent salt, which does not crystallize, and which is decomposed, leaving magnesia when exposed to ignition.+
- 8. Bromide of aluminum. When the vapour of bromine is passed over a mixture of alumina and charcoal at a red heat bromide of aluminum is formed. It dissolves in water, and with difficulty yields crystals, which have a very astringent taste, redden litmus paper, and when heated to redness undergo decomposition, pure alumina remaining behind.
- 9. Bromide of glucinum. Glucinum burns when heated in vapour of bromine. The bromide of glucinum sublimes in long white needles, easily soluble in water, and fusible when heated. The solution in water is accompanied by a copious evolution of heat.
- 10. Bromide of thorium. The solution of hydrated thorina in an excess of aqueous hydrobromic acid when left to spontaneous evaporation leaves a tough gum, which, owing to the decomposition of the superabundant hydrobromic acid assumes a deep yellow colour.§
  - 11. Bromide of iron. Described in Vol. I. p. 492.

Iron dissolves readily in hydrobromic acid with the evolution of hydrogen gas. The solution is light green, when properly concentrated it deposites rhombic tables, which acquire a deep colour, and undergo partial decomposition by exposure to the air. The constituents of this salt, according to Löwig, are

1 atom bromine		•	•	•	10
1 atom iron	•	•		•	3.5
6 atoms water		•	•	•	6.75
					90.95

12. Sesquibromide of iron. According to Löwig, when bromide of iron is heated with bromine it unites with an additional half atom of that substance, and forms a brownish red mass, which fuses at a moderate heat, and when sublimed has a close resemblance to mosaic gold, while a portion of vapour of bromine is dissipated and bromide of iron remains. This sesquibromide dissolves in water, and forms a yellowish brown

<sup>\*</sup> Löwig. + Balard, Ann. de Chim. et de Phys. xxxii. 359.

<sup>‡</sup> Löwig. § Berzelius.

liquid which will not crystallize. When the solution is evaporated to dryness partial decomposition takes place.

- 13. Bromide of manganese. When carbonate of manganese is dissolved in hydrobromic acid, and the solution evaporated to dryness, a light red powder remains. When this powder is heated in a glass tube with a narrow mouth it assumes a light rose red colour. When ignited it undergoes fusion. When exposed to the air it is decomposed into vapour of bromine and protoxide of manganese.\*
- 14. Bromide of zinc. Aqueous hydrobromic acid readily dissolves zinc with the evolution of hydrogen gas. When the colourless solution is concentrated it deposites small crystals, which melt when heated, and if the heat be applied in a glass tube with a narrow orifice bromide of zinc sublimes in white needles, which may be melted into a light yellow liquid. They speedily deliquesce in the air.+
  - 15. Bromide of lead. Described in Vol. I. p. 564.
  - 16. Bromide of tin. Described in Vol. I. p. 576.

Tin dissolves in concentrated hydrobromic acid by the assistance of heat with the evolution of hydrogen gas. solution is colourless and reddens litmus paper. When evaporated it does not deposite crystals, but becomes gelatinous. When farther heated it becomes a grayish white mass with considerable lustre, fusing when heated into a yellowish oil. ‡

17. Bibromide of tin. Described in Vol. I. p. 577.

18. Bromide of copper. Oxide of copper dissolves readily in hydrobromic acid. The dilute solution is emerald green, the concentrated solution brown. By evaporation it yields right rectangular prisms, which melt when gently heated, and lose their water of crystallization. The dry mass dissolves readily in water, and deliquesces when exposed to the air. The constituents of the crystals, according to the analysis of Löwig, are

1 atom bromine	•	•	. •	10
1 atom copper	•		•	4.
5 atoms water	•	•	•	5.625
				19.625

19. Dibromide of copper. When fine copper wire is heated to redness in contact with bromine vapour, a combination takes From this compound water dissolves out bromide of

Class III. copper. Hydrobromic acid dissolves out the dibromide, while metallic copper remains behind. Water throws down the dibromide. It is a white powder, which when fused at a red heat becomes gravish brown. It is not volatile in close vessels, and with difficulty in the open air.\*

- 20. Bromide of bismuth. Described in Vol. I. p. 608.
- 21. Bromides of mercury. Described in Vol. I. p. 620.
- 22. Bromide of silver. Described in Vol. I. p. 633.
- 23. Bromide of gold. Described in Vol. I. p. 645.

Bromide of gold dissolves readily in water. The solution has a dark cinnabar red colour, and by concentration it may be made to deposite crystals having the same colour. The colouring power of these crystals is so great, that one part gives a sensible tinge to 5000 parts of water. Reagents act upon it in the same way as on a solution of chloride of gold.+ It gives a violet colour to animal substances.

- 24. Bromide of platinum. Described in Vol. I. p. 664.
- 25. Sesquibromide of arsenic. Described in Vol. I. p. 308.
- 26. Sesquibromide of antimony. Described in Vol. I. p. 324.
- 27. Bromide of chromium. When chromate of lead is agitated in aqueous hydrobromic acid, and after filtration the liquid is boiled for some time, a dark green solution is obtained, which does not yield crystals. When the solution is evaporated to dryness and the residue exposed to a red heat, a yellowish red powder remains, which, according to Löwig, is a sesquibromide of chromium.
- 28. Terbromide of chromium. Obtained by mixing chromate of potash and bromide of potassium with sulphuric acid and distilling. The matter distilled over always contains free bromine. Its colour is pretty deep. When dissolved in water it undergoes decomposition.

# SECTION II.-OF BROMO-HYDRARGYRATES.

This genus of salts, as well as the other kindred genera, is still almost unexplored, only one or two of them being known, which were pointed out by Löwig.

1. Bromo-hydrargyrate of ammonia. Hydrobromate of ammonia dissolves bromide of mercury. When aqueous bromide of mercury is mixed with ammonia, a white precipitate falls, which Löwig has shown to contain mercury, bromine, and ammonia.

2. Bibromo-hydrargyrate of potassium. A warm concentrated solution of 1 atom of bromide of potassium dissolves more than 3 atoms of bromide of mercury. It becomes stiff and opaque, and when allowed to cool, or when diluted with water, it retains only 2 atoms in solution. When this solution is again concentrated, it deposites yellow coloured octahedrons, composed, according to the analysis of Löwig, of

2 atoms bromide of mercury . 22.5 1 atom bromide of potassium . 15

When these crystals are heated, they melt without giving off any water, and the bromide of mercury sublimes. When a greater quantity of water is employed, half the bromide of mercury precipitates.\*\*

## CLASS IV.

## IODINE ACID SALTS.

The investigation of this class of salts has not made much greater progress than the preceding, though the same difficulties do not oppose themselves to the study of them, iodine being now prepared in large quantity, and at a sufficiently cheap rate for the use of the medical practitioner.

### SECTION I .-- OF HYDRIODATES AND IODIDES.

The same uncertainty respecting the existence of hydriodates, which was noticed with respect to hydrochlorates and hydrobromates, still obscures this department of chemistry. But the analogy is so complete, that whatever conclusion we come to respecting one of these classes of salts, will apply to them all.

1. Hydriodate of ammonia. This salt is formed when equal volumes of hydriodic acid and ammoniacal gas are mixed together. The easiest way of obtaining it is to dissolve liquid ammonia in hydriodic acid. It crystallizes in cubes. It is very soluble in water, and deliquesces when exposed to the air. It may be sublimed in close vessels without decomposition. But in the open air it is partially decomposed when sublimed,

and it becomes coloured. But it may be rendered colourless again by exposure to the open air, or by the addition of a little ammonia.\* Its constituents are

1 atom hydriodic acid . 15.875
1 atom ammonia . 2.125

2. Iodide of potassium. Described in vol. i. p. 403.

Serullas has suggested the following plan, as yielding a very pure iodide of potassium. Pous upon iodine, previously washed, 15 times its weight of alcohol of the specific gravity 0.897. Throw into this solution, by small portions at a time, the alloy of potassium and antimony,† stirring the liquid well after every addition with a glass rod. When the liquid has become perfectly colourless, filter and evaporate in a gentle heat.‡ The salt crystallizes usually in cubes, sometimes in octahedrons, or different modifications of these forms. The taste is a strong bitter, which continues long in the throat. In a moist atmosphere it deliquesces. It is very soluble in water, and its solubility at different temperatures is as follows:

100 water at 54°.5 dissolve 136% of the salt.

61 141 || 64 · 5 143 || 248 221 \*\*

At 54°·5 it dissolves in  $5\frac{1}{2}$  times its weight of alcohol of the specific gravity 0·850, and in 39 or 40 times its weight of absolute alcohol at the temperature of 56°. It is much more soluble in hot alcohol, and crystallizes in needles as the solution cools. The constituents of this salt are

3. Iodide of sodium. This salt may be formed in the same way as the preceding. It crystallizes in flat rhomboids, which uniting together form larger crystals, somewhat similar to those of sulphate of soda. It contains much water of crystallization, and notwithstanding is very deliquescent. †† When heated it

<sup>\*</sup> Gay-Lussac, Ann. de Chim. xci. p. 62.

<sup>†</sup> Formed by heating tartar emetic first in the air, and then exposing the residue to a strong heat in a covered crucible.

<sup>‡</sup> Ann. de Chim. et de Phys. xx. 164. § Baup. || Ibid. ¶ Gay-Lussac. || \*\* Ibid. †† Ibid.

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melts, and after losing its water of crystallization may be made to undergo the igneous fusion like common salt. Its constituents, (abstracting the water, which has not been determined), are

1 atom iodine 1 atom sodium	•	•	15·75 3
		_	19.75

4. Iodide of barium. It is easily obtained by dissolving carbonate of barytes in hydriodic acid. It crystallizes in fine prisms similar in appearance to muriate of strontian. It is very soluble in water, and but feebly deliquescent. When long exposed to the air, a portion of the hydriodic acid is decomposed and dissipated, carbonate of barytes is formed, and hydriodate of barytes coloured by iodine may be dissolved by water. In close vessels it may be heated to redness without undergoing any alteration. But if air or oxygen gas have access to it while red hot, vapours of iodine are exhaled, and the salt becomes alkaline.\* Its constituents are

1 atom iodine	•	•	15.75
1 atom barium	•	•	8.5
1 atom water	•	•	1.125
•			25:375

- 5. Iodida of strontium. This salt is very soluble in water. It fuses when heated to a temperature rather below redness. This fusion produces little alteration in close vessels; but in the open air vapours of iodine are exhaled, and the salt becomes alkaline+
- 6. Iodide of calcium. This salt is obtained in a state of purity by saturating hydriodic acid with carbonate of lime. It is very soluble in water and very deliquescent. It may be dried in the air without undergoing decomposition.‡
- 7. Iodide of magnesium. This salt is deliquescent and crystallizes with difficulty. When heated to redness, out of the contact of air, the acid flies off and leaves the magnesia.
- 8. Iodide of glucinum. Glucinum, when heated in vapour of iodine, takes fire, and an iodide sublimes in white needles.
  - 9. Iodide of iron. Described in vol. i. p. 493.
  - 10. Iodide of nickel. Described in vol. i. p. 532.

	n. de Chim. xci. 57.	† Ibid. p. 60.
‡ Ibid.		§ Ibid. p. 63.
	•	•

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- 11. Iodide of cobalt. This salt dissolves in water with a red colour.
- 12. Iodide of zinc. This salt is easily obtained by heating iodine with an excess of zinc under water. The liquid at first acquires a deep brown colour; but if we continue the heat, more zinc is dissolved, and the whole becomes at last as colourless as water. It cannot be crystallized by evaporation. But if it be evaporated to dryness and fused, it crystallizes in beautiful prisms similar to those of white oxide of antimony. When thus heated, it is anhydrous indide of zinc. When heated in the open air it is decomposed, the acid is driven off under the form of iodine, and oxide of zinc remains.\* The constituents of this salt are as follows:

1	atom	iodine	•	•	15.75
1	atom	zinc	_	_	4.25

20

- 13. Iodide of cadmium. Described in vol. i. p. 556.
- 14. Iodide of lead. Described in vol. i. p. 565.
- 15. Iodide of tin. Described in vol. i. p. 577.
- 16. Iodide of copper. Described in vol..i. p. 594.
- 17. Iodide of bismuth. Described in vol. i. p. 608.
- 18. Iodides of mercury. Described in vol. i. p., 620.
- 19. Iodide of silver. Described in vol. i. p. 633.
- 20. Iodide of gold. Described in vol. i. p. 645.
- 21. Iodide of arsenic. Described in vol. i. p. 308.
- 22. Iodide of antimony. See vol. i. p. 324.
- 23. Iodides of molybdenum. See vol. i. p. 359.

## SECTION II. -- OF IODO-STANNATES.

From the experiments of Boullay it appears that iodide of tin dissolves in aqueous solutions of hydriodate of ammonia, iodides of potassium, sodium, barium, and strontium.

# SECTION III. -- OF IODO-PLUMBATES.

Boullay has also observed that iodide of lead dissolves in the aqueous solution of iodide of potassium, and the solution, when concentrated, crystallizes in needles.

<sup>\*</sup> Gay-Lussac, Ann. de Chim. xci. p. 65.

<sup>†</sup> Ann. de Chim. et de Phys. xxxiv. 372.

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#### SECTION IV. -- OF IODO-HYDRARGYRATES.

A few of these salts have been examined by Bonsdorf. The following are the results which he obtained.

- 1. Iodo-hydrargyrate of potassium. This salt may be obtained by saturating a cold solution of iodide of potassium with iodide of mercury, and abandoning the solution to spontaneous evaporation. It crystallizes in needles, which deliquesce in a moist atmosphere.\*
- 2. Iodo-hydrargyrate of sodiem. It may be obtained in the same way as the preceding salt. It crystallizes in rhomboidal prisms, has a saffron yellow colour, and speedily deliquesces when exposed to the air.+
- 3. Iodo-hydrargyrate of iron. This salt may be prepared like the preceding, but must not be exposed to the air, because it is decomposed when evaporated in contact with the atmosphere. It crystallizes in fine yellow prisms, which gradually becomes covered with a brown rust.
- 4. Iodo-hydrargyrate of zinc. It crystallizes in six-sided prisms, terminated by acute pyramids. It deliquesces even in a dry atmosphere.

#### CLASS V.

### FLUORINE ACID SALTS.

As fluorine has not hitherto been obtained in a separate state, it is still to be regarded as a hypothetical substance. I have stated in the first volume of this work (p. 88.) the reasons which have induced chemists to admit its existence. And in vol. ii. p. 197, I have given an account of the different acids into which this principle enters as a constituent; our object in this place is to describe the different genera of salts which these acids form with the various salifiable bases.

SECTION I .-- OF FLUORIDES, HYDRO-FLUATES, OR FLUATES.

The properties of the acid called fluoric or hydro-fluoric ||

\* Ann. de Chim. et de Phys. xliv. p. 262. † Ibid. ‡ Ibid. \$ Ibid. ¶ From the opinion that it is a compound of

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acid have been detailed in vol. i. p. 87. The salts which it forms were first examined by Gay-Lussac and Thenard,\* and more lately by Berzelius.† They have received different names, according to the opinion entertained respecting the nature of the acid which they contain. Those who consider it as a compound of a combustible base and oxygen, call these salts fluates; those that consider the acid as a compound of fluorine and hydrogen call them hydro-fluates; while those who are of opinion that fluorine is analogous to oxygen, and that when hydrofluoric acid comes in contact with a base a double decomposition takes place, (fluorine uniting with the base, while the oxygen and hydrogen form water), give them the appellation of fluorides. This last opinion is by far the most plausible; though it would be too much to affirm that it has been completely demonstrated.

- Sp. 1. Hydro-fluate of ammonia. This salt may be obtained by the following process, for which we are indebted to Berzelius. Mix in a platinum crucible 1 part of sal ammoniac and  $2\frac{1}{4}$  parts of fluoride of sodium, both quite dry and in powder. Cover the crucible with an inverted lid filled with cold water. Apply a gentle heat. The hydro-fluate of ammonia sublimes and attaches itself to the lid of the crucible in the state of small prisms. It is not altered by exposure to the air. It is abundantly soluble in water, slightly in alcohol. When heated it melts before it begins to sublime. It corrodes glass vessels even when dry. ‡
- 2. Bihydro-fluate of ammonia. It may be obtained in granular crystals by saturating hydro-fluoric acid with ammonia and evaporating at the temperature of 100°. Half the ammonia escapes, and the bisalt remains in granular crystals. When heated it may be volatilized in thick white vapours. It precipitates the solutions of all the alkaline earths, and earths proper, in acids, because fluoric acid forms insoluble compounds with all the earths. §
- 3. Fluoride of potassium. It may be obtained by saturating bicarbonate of potash with hydro-fluoric acid, and after evaporating to dryness, exposing the residue to a red heat. This salt has a very sharp taste, crystallizes with difficulty, in cubes or rectangular prisms, is very deliquescent, and of course very soluble in water. When heated it undergoes first the aqueous

<sup>\*</sup> Recherches Physico-Chimiques, ii. I.

<sup>†</sup> Kong. Vet. Acad. Handl. 1823, p. 284. 

‡ Berzelius, ibid. p. 298.

<sup>§</sup> Gay-Lussac and Thenerd, Recherches Physico-chimiques, ii. p. 23.

and then the igneous fusion. Sulphuric acid decomposes it, sedriving off fluoric acid in vapour.\*

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4.\* Bifluoride of potassium. It may be obtained by dissolving potash in an excess of fluoric acid, and concentrating the solution. By spontaneous evaporation it crystallizes in rectangular tables with bevelled edges, or in cubes. It is very soluble in water. When heated it melts, gives off its excess of acid, and again becomes solid. From the experiments of Berzelius, its constituents appear to be

2 atoms fluorine	•	•	4.5
1 atom potassium	•	•	5
2 atoms water	•	•	2.25
			11.75+

- 5. Fluoride of sodium. This salt may be prepared most economically by mixing 100 parts of dry fluo-silicate of soda and 112 parts of anhydrous carbonate of soda with as much water as will reduce the whole to a thin pap, and boiling till all effervescence is over. When the whole has concreted to a solid mass, let it be pounded and boiled in water, to dissolve out the fluoride of sodium. By evaporation the salt is obtained in cubes and regular octahedrons. The crystals are transparent and have sometimes a pearly lustre. The salt is less fusible than glass. Water dissolves it very slowly. At 61° 100 parts of water dissolve only 4 parts of this salt. It is insoluble in alcohol.‡
- 6. Bifluoride of sodium. It crystallizes in transparent rhomboids, has a sharp and acid taste, and is sparingly soluble in water. Its constituents are

2 atoms fluorine	•	•	4.5
1 atom sodium	•	•	3
2 atoms water	•	٠.	$2 \cdot 25$
			9.75

7. Fluoride of lithium. This salt dissolves with difficulty in water, resembling in that respect carbonate of lithia. The solution is converted by evaporation into a white mealy looking mass, composed of opaque granules.

<sup>\*</sup> Gay-Lussac and Thenard, Recherches, Physico-chimiques, ii. p. 18-

<sup>§</sup> Ibid. p. 294.

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The biflupride of lithium is a crystallizable salt, but little soluble in water.\*

8. Fluoride of barium. It is most easily formed by digesting newly precipitated carbonate of barytes in an excess of fluoric acid. A white powder remains, which constitutes the salt. It is tasteless, and only very slightly soluble in water, even when acidulated with fluoric acid. But it dissolves abundantly in muriatic acid, and ammonia precipitates from the solution a double salt, composed of

9. Fluoride of strontium. May be prepared in the same way as the preceding salt, which it closely resembles.

10. Fluoride of calcium. This is the well known mineral, distinguished by the name of fluor spar. When pure it is transparent and colourless, and crystallized in cubes and octahedrons, or modifications of these forms. It is tasteless and insoluble in water, and has a specific gravity of 3·15.

When heated it decrepitates and phosphoresces strongly in the dark. It emits this light even under water, or in the vacuum of an air-pump. When kept hot for some time, it ceases to shine, and the phosphorescent property cannot be again restored to it by any process known, except by decomposing it altogether by means of sulphuric acid, and forming it anew. Scheele ascertained that new-formed fluate of lime is equally phosphorescent with native. The cause of this curious property is not well understood. After being heated, the salt, though it refuses to phosphoresce any more, has not lost any perceptible weight, nor is it altered in any of its other qualities. When strongly heated, this salt melts into a transparent glass. According to Saussure, this takes place at the temperature of 51° Wedgewood.‡

Sulphuric acid incorporated with fluor spar in fine powder, converts it into a transparent syrupy mass, which may be drawn into threads; but no fluoric acid is expelled till the mixture is heated to about 100°. But if the spar contains the slightest admixture of silica, it instantly effervesces when mixed with sulphuric acid. The constituents of this salt are

1 atom fluorine . . 2.25 1 atom calcium . . 2.5

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4.75

- · 11. Fluoride of magnesium. Carbonate of magnesia dissolves with effervescence in fluoric acid. The fluoride is a tasteless white powder, insoluble in water, and scarcely soluble in acids. When this salt is formed by pouring oxide of potassium into sulphate of magnesia, it precipitates at first in a gelatinous form, and is then soluble in acids; but as soon as it dries it becomes insoluble in these bodies.\*
- 12. Fluoride of aluminum. Very soluble in water. A solution of it, when concentrated, forms a clear uncrystallizable syrup, which, by evaporation, leaves the salt in a state resembling gum arabic. In this state it is tasteless, and appears at first insoluble in water; but in about an hour it is completely dissolved, and it dissolves still more rapidly in hot water. When ignited, a subsalt is left.†
- 13. Fluoride of glucinum. Obtained by mixing solutions of fluoride of potassium and muriate of glucina. A jelly precipitates, which dissolves in hot water, and precipitates in small crystals as the liquid cools.‡
- 14. Fluoride of yttrium. Nearly insoluble in water, however, before ignition, it has an astringent taste, and reddens moistened litmus paper.§
- 15. Fluoride and sesqui-fluoride of cerium correspond in most of their characters with fluoride of yttrium. Both occur native. The sesqui-fluoride of cerium has a yellow colour.
- 16. Fluoride of zirconium. Very soluble in water. When the solution is evaporated it deposites crystals, which, when washed with water, are converted into a subsalt.
- 17. Fluoride of thorium. A white heavy powder, insoluble in water, and not decomposed by exposure to a red heat.
- 18. Fluoride of iron. It may be obtained by dissolving the metal in hydro-fluoric acid by a gentle heat. The salt gradually separates in small crystals, which appear to be rectangular four-sided tables. It is at first white, but acquires a yellow shade by exposure to the air. Water dissolves it sparingly. When ignited, it loses water and a portion of acid, becomes red, and sustains no further decomposition.
  - \* Gay-Lussac and Thenard; Recherches Physico-chimiques, ii. 26.
  - † Ibid. p. 27. ‡ Ibid. p. 27. § Berzelius; ubi supra, p. 302.
  - | Ibid. | Ibid. p. 304.

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- 19. Sesqui-fluoride of iron. It may be obtained in the state of a flesh coloured powder, by dissolving the hydrated peroxide of iron in fluoric acid, and evaporating. Taste sweet and astringent. Water dissolves it slowly, but completely. The solution is colourless, even after adding ammonia, which, when mixed in excess, throws down a subsalt.\*
- 20. Fluoride of manganese: A white crystalline powder, permanent in a red heat, and soluble in water when assisted by an excess of acid.+
- 21. Sesqui-fluoride of manganese. The hydrated native oxide of manganese dissolves in fluoric acid with an intense red colour, and by spontaneous evaporation the liquid deposites transparent prismatic crystals of a ruby red or brown colour, according to the size. It dissolves in a minimum of water without decomposition; but when the solution is heated or diluted, a subsalt precipitates.
- 22. Fluoride of nickel. Formed by dissolving carbonate of nickel in fluoric acid. A light green coloured powder, sparingly soluble in water, and decomposed, a subsalt being precipitated, when mixed with an excess of water.§
- 23. Fluoride of cobalt. Similar to the preceding salt, except that its colour is rose red.
- 24. Fluoride of zinc forms small white opaque crystals, difficultly soluble in water, but abundantly soluble in ammonia.
- 25. Fluoride of cadmium. When the solution of this salt is evaporated, it is obtained in a white crust, which shows no symptoms of regular crystallization.\*\*
- 26. Fluoride of lead. Fluoric acid has no sensible action on lead. But when the acid is dropped into a solution of acetate of lead, fluoride of lead precipitates in brilliant plates. It acts feebly as an acid on paper stained with litmus. It is insoluble in water, but very soluble in nitric, muriatic, and fluoric acids. It melts when heated to redness, and becomes yellow, losing a portion of its acid. Sulphuric acid decomposes it, disengaging vapours of fluoric acid. ††
- 27. Fluoride of tin. It is soluble in water, and crystallizes in white shining opaque prisms. It is rapidly peroxidized by exposure to the air.‡‡

<sup>\*</sup> Berzelius; ubi supra, p. 304. † Ibid. p. 303. ‡ Ibid. § Ibid. p. 305. † Ibid. ¶ Ibid.

<sup>\*\*</sup> Ibid.

<sup>††</sup> Gay-Lussac and Thenard; Recherches Physico-chimiques, ii. 34.

<sup>‡‡</sup> Berzelius, ibid. p. 308.

Sect. I.

- 28. Subfluoride of copper. It may be formed by treating the subhydrate of copper with fluoric acid. It instantly becomes red, and does not dissolve in an excess of the acid. When ignited, it assumes a dark cinnabar colour. When exposed in a moistened state to the air, it gradually absorbs oxygen, and becomes green.\*
- 29. Fluoride of copper. Fluoric acid readily dissolves the oxide of copper, provided there be an excess of acid. When the liquid is evaporated, small blue-coloured crystals are deposited. Sulphate of copper is not precipitated by fluoride of potassium, unless it constitute a concentrated solution.
- 30. Fluoride of mercury. When red oxide of mercury in fine powder is digested in fluoric acid, it is changed into a light orange yellow powder, which forms a colourless solution in water, and crystallizes in dark yellow prisms. Water decomposes these crystals, and forms a subsalt similar in appearance to turpeth mineral. The neutral salt sublimes in a red heat, and forms yellow coloured crystals. In a glass retort it is instantly decomposed.‡

Berzelius could not succeed in obtaining a sub-fluoride of mercury, analogous to calomel.

- 31. Fluoride of silver. Fluoric acid readily dissolves the oxide of silver. The fluoride has a strong metallic taste, very soluble in water, and does not crystallize. It is very volatile. When heated it melts, loses its excess of acid, but still continues soluble in water. It blackens the fingers. It is precipitated by muriatic acid. All the bases precipitate the fluoric acid from it except ammonia. This salt cannot be formed by the direct action of fluoric acid on silver. But it is formed when fluoride of mercury is made to act upon silver. Fluoride of potassium does not occasion a precipitate in nitrate of silver.§
- 32. Fluoride of platinum. This salt may be obtained by mixing fluoride of potassium with a solution of chloride of platinum, evaporating the mixture to dryness, and treating the residue with alcohol, which dissolves fluoride of platinum, leaving chloride of potassium untouched. The alcoholic solution when mixed with water, and left to spontaneous evaporation, is gradually converted into a yellow coloured uncrystallizable mass. It forms a double salt with fluoride of potassium.

<sup>\*</sup> Berzelius, Recherches Physico-chimiques, ii. p. 306.

<sup>†</sup> Gay-Lussac and Thenard, ii. p. 32. ‡ Ibid. p. 309. § Ibid. p. 33.

Berzelius, ubi supra, p. 310.

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- 33. Fluoride of antimony is very soluble in water, and may be obtained in colourless crystals, by spontaneous evaporation. It has a taste similar to that of tartar emetic.\*
- 34. Fluoride of chromium. A green crystalline mass, easily soluble in water.+
  - 35. Bifluoride of chromium has a pale rose red colour. ‡
- 36. Bifluoride of uranium. A white pulverulent salt, readily soluble in water, with a yellow colour.

#### SECTION II. --- OF FLUO-BORATES.

For the examination of almost every one of the fluo-borates hitherto described, we are indebted to the industry of Berzelius.

1. Fluo-borate of ammonia. Fluo-boric acid and ammonia unite in three proportions; the first salt is a compound of 1 volume fluo-boric acid gas, and 1 volume ammoniacal gas. Hence its constituents by weight are

2 atoms fluo-boric acid	•	•	<b>8·5</b>
1 atom ammonia	•	•	$2 \cdot 125$
			10.625

The second salt is a compound of 1 volume fluo-boric acid + 2 volumes ammoniacal gas. Hence its constituents are

l atom fluo-boric acid	•	•	4.25
l atom ammonia	•	•	$2 \cdot 125$
			6.375

The third salt is a compound of 1 volume fluo-boric acid + 3 volumes ammoniacal gas. Hence its constituents are

1 atom fluo-boric acid 1 atom ammonia	•	•	4·25 3·1875
•			
			7.43758

When boracic acid is introduced into a neutral solution of hydro-fluate of ammonia, it is dissolved, while at the same time ammonia is disengaged. If just the requisite quantity of acid is employed, a neutral fluo-borate of ammonia is formed. The dry salt may be sublimed without undergoing decomposition. Its taste resembles that of sal ammoniac, and it reddens litmus paper. It is very soluble both in water and alcohol.

<sup>\*</sup> Berzelius, ubi supra, p. 308.

<sup>†</sup> Ibid. ‡ Ibid.

<sup>§</sup> John Davy, Phil. Trans. 1812, p. 368.

<sup>||</sup> Berzelius, Kong. Vet. Acad. Handl, 1824, p. 75.

Sect. II.

- 2. Fluo-borate of potash. When fluoride of potassium is mixed with borate of potash, this salt falls as a gelatinous precipitate. When dried it forms a white mealy powder. Its taste is slightly bitter, and it does not redden litmus paper. It is anhydrous. 100 parts of cold water dissolve 1.42 of this salt. But boiling water dissolves it much more abundantly. It is slightly soluble in boiling alcohol. When heated it fuses, and gives off fluo-boric gas, but requires a high and long continued heat to decompose it. It dissolves in boiling-hot solutions of the alkalies and their carbonates, and as the solution cools, it crystallizes again unaltered.\*
- 3. Fluo-borate of soda. It crystallizes in large transparent four-sided rectangular prisms. It has a bitterish and weakly acid taste, and strongly reddens litmus paper. It is anhydrous, pretty soluble in water, and sparingly soluble in alcohol.+
- 4. Fluo-borate of lithia. It is obtained by precipitating fluo-borate of barytes with sulphate of lithia. It is very soluble in water, tastes like the preceding salt, and crystallizes in large prisms. In a moist atmosphere it deliquesces.‡
- 5. Fluo-borate of barytes. It may be formed by adding carbonate of barytes in small quantities at a time to fluo-boric acid, till it ceases to be dissolved. By spontaneous evaporation the salt crystallizes in four-sided rectangular prisms. It acts as an acid on vegetable blues, but has the usual taste of barytes salts. At the temperature of 104° it effloresces. Alcohol decomposes it. The crystals contain 10.34 per cent. of water. Hence the constituents are probably

		•			15.43758
$1\frac{1}{2}$	atom	water	•	•	1.6875
1	atom	barytes	•	•	9.50
1	atom	fluo-boric acid	•	•	4.25

- 6. Fluo-borate of lime. A gelatinous mass which has an acid taste, and reddens litmus paper.
- 7. Fluo-borate of magnesia. Very soluble in water, and forms large prismatic crystals. Its taste is bitter.¶
- 8. Fluo-borate of alumina. It is only soluble in water when there is an excess of acid present. By slow evaporation it may be obtained in crystals.\*\*

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1824, p. 72. † Ibid. p. 74. † Ibid. p. 76. | Ibid. p. 77. ¶ Ibid. \*\* Ibid.

Class V.

- 9. Fluo-borate of yttria. Similar to the preceding salt in its characters.\*
- 10. Fluo-borate of zinc. It may be obtained by dissolving zinc filings in fluo-boric acid. It does not crystallize, and is deliquescent.+
- 11. Fluo-borate of lead. Crystallizes in four-sided tables, similar to the form of fluo-borate of barytes. Its taste is at first sweet and astringent, but it finally leaves an impression of acidity. Both water and alcohol decompose it, at least partially.
- 12. Fluo-borate of copper. It is very soluble in water, and when evaporated, yields fine blue needle form crystals, which are very deliquescent.

#### SECTION III. -- OF FLUO-SILICATES.

These salts, which have hitherto been examined by Berzelius only, seem analogous to the hypo-sulphates, sulpho-vinates, sulpho-naphthalates, &c.

1. Fluo-silicate of ammonia. This salt is easily formed by distilling a mixture of fluo-silicate of potash and sal ammoniac. It sublimes in an uncrystalline mass. But if it be dissolved in water and left to spontaneous evaporation, it forms large transparent crystals. Its primary form is the rhomboid, but it has a strong tendency to shoot into six-sided prisms. It is very soluble in water. When heated it decrepitates slightly, and sublimes unaltered.

Gay-Lussac and Dr. John Davy have shown that when one volume of fluosilicic acid and 2 volumes of ammoniacal gas are mixed the gases condense into this salt. Hence it is a compound of

1 atom fluosilicic acid	•		6.5
l atom ammonia	•	•	2.125
			0.005

2. Fluo-silicate of potash. If into fluo-silicic acid dissolved in water a quantity of potash, or the carbonate, sulphate, nitrate, or muriate of that alkali, be dropped, a gelatinous precipitate immediately appears, which, when dried, becomes white like chalk, and separates into small loose grains like the sand of an hour-glass. This powder is a combination of fluo-silicic acid and potash. Its nature was first ascertained by Scheele.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1824, p. 77. † Ibid. p. 78. † Ibid. § Ibid.

It has an acid taste, and is soluble in about 150 parts of Sect. III. boiling water, but is again partly deposited as the solution cools. When strongly heated it melts into a transparent glass and loses its acid.\*

- It is rather more soluble in boiling than in cold water, and if a saturated solution be evaporated the salt may be obtained in small crystals, which are sometimes rhombs and sometimes six-sided prisms. The crystals are anhydrous.+
- 3. Fluo-silicate of soda. This salt possesses similar characters with the preceding. It is, however, heavier, and forms larger granules. It has a gelatinous appearance while moist, but becomes a mealy powder when dried. It is pretty soluble in water, and shoots into crystals which seem to be regular sixsided prisms. These crystals are anhydrous. When heated it behaves in the same way as the preceding salt.‡
- 4. Fluo-silicate of lithia. It is almost insoluble in water. The solubility is augmented by an excess of acid, and it may be obtained by this means in small transparent six-sided prisms, obviously derived from a rhomboid. When heated it melts, and obstinately retains its acid.§
- 5. Fluo-silicate of barytes. It is best obtained by mixing a solution of chloride of barium with the liquid acid. After a few minutes it precipitates in minute crystals, and the liquid contains disengaged muriatic acid. Nearly the whole barytes may be precipitated by this means, and the precipitation is not prevented by an excess of muriatic acid. The crystals of this salt are prisms with very long acuminations. The crystals are anhydrous. When heated the salt is decomposed, and fluoride of barium remains.
- 6. Fluo-silicate of strontian. This salt is pretty soluble in water, and may be obtained in large slightly oblique four-sided prisms. They contain water of crystallization, and become enamel white when heated. Water decomposes it, at least partially.
- 7. Fluo-silicate of lime. It may be obtained by digesting a mixture of pulverized fluor spar and silica in muriatic acid. But the easiest process is to add carbonate of lime to the liquid acid so long as it continues to dissolve. It is insoluble in water, unless when assisted by an excess of acid, and it crystallizes as the excess evaporates. The crystals are oblique four-sided

<sup>\*</sup> Scheele, Crell's Annals, i. 214. Eng. Trans.

<sup>†</sup> Berzelius, Kong. Vet. Acad. Handl. 1823, p. 336.

<sup>1</sup> Ibid. p. 338.

<sup>§</sup> Ibid. p. 339.

<sup>|</sup> Ibid. p. 341.

<sup>¶</sup> Ibid. p. 342.

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- prisms. When digested in water the salt is partially decomposed, fluoride of calcium and silica being precipitated, while fluo-silicic acid remains dissolved in the water.\*
- 8. Fluo-silicate of magnesia. A transparent yellowish gum-my looking mass, easily soluble in water.+
- 9. Fluo-silicate of alumina. A clear colourless jelly, which when dried splits into fragments and appears yellowish, but still retains its transparency. It dissolves slowly, but completely in water.
- 10. Fluo-silicate of glucina is readily soluble in water, and is converted by evaporation into a colourless syrup, which finally becomes white and opaque. Its taste is astringent without any mixture of sweetness.§
- 11. Fluo-silicate of yttria. It is insoluble in water, but dissolves in an excess of acid.
- 12. Fluo-silicate of zirconia dissolves very easily in water, and may be obtained in white crystals having a pearly lustre. The solution becomes opaque when boiled, but most of the salt remains dissolved.
- 13. Fluo-silicate of iron. When a solution of this salt prepared by dissolving iron filings in the liquid acid, is allowed to evaporate in an iron basin, it crystallizes in green coloured six-sided prisms, but it is difficult to obtain regular crystals.\*\*
- 14. Fluo-silicated peroxide of iron. A semitransparent pale flesh coloured, gummy mass. It dissolves in water, and the solution is slightly coloured.++
- 15. Fluo-silicate of manganese. Very soluble in water. It crystallizes in long small regular six-sided prisms. Primary form a rhomboid. Crystals very slightly amethyst red. By ignition it is converted into fluoride of manganese without losing its crystalline form.‡‡
  - 16. Fluo-silicate of nickel. These salts dissolve readily in
- 17. Fluo-silicate of cobalt. \( \) water. Their crystals are the same as those of fluo-silicates of iron and manganese. The salt of nickel is green, while that of cobalt is red.\( \)\( \)\( \)
- 18. Fluo-silicate of zinc. It may be obtained by dissolving zinc in the acid liquor. It is exceedingly soluble in water. It crystallizes in three-sided equiangular prisms. The crystals are not altered by exposure to the air.
  - \*\* Berzelius, Kong. Vet. Acad. Handl. 1823, p. 341. † Ibid. p. 343. † Ibid. § Ibid. || Ibid. ¶ Ibid. \*\* Ibid. p. 344. †† Ibid. p. 343. \$\sqrt{1}\$ Ibid. p. 343. \$\sqrt{1}\$ Ibid. p. 343. \$\sqrt{1}\$ Ibid. p. 343.

Sect. III.

19. Fluo-silicate of cadmium. It is very soluble in water, and crystallizes in long colourless prisms which contain water of crystallization.\*

20. Fluo-silicate of lead. A transparent gummy like mass, soluble in water, and having the sweet taste of salts of lead.+

- 21. Fluo-silicate of tin. It is very soluble in water, and crystallizes in long prisms. But it is partially oxidized and decomposed during evaporation, and the oxide thus formed precipitates in the state of a silicate.‡
- 22. Fluo-silicate of suboxide of copper. It has a red colour and closely resembles subfluoride of copper. In a high temperature it melts and loses its fluo-silicic acid.§
- 23. Fluo-silicate of mercury is soluble only in an excess of acid, and crystallizes by evaporation in small needles having a very slight tinge of yellow. When put into water it is partly converted into a yellow insoluble subsalt. When ignited fluo-silicic acid escapes, and the fluoride of mercury undergoes decomposition in the way formerly explained. The yellow subsalt is blackened by ammonia, but is again rendered lighter by the addition of water.
- 24. Fluo-silicated suboxide of mercury may be prepared by digesting newly prepared suboxide while still moist in the liquid acid. It is converted into a pale straw yellow powder. The solution of the salt has a weak metallic taste, and is copiously precipitated by muriatic acid.
- 25. Fluo-silicate of silver. It is a very deliquescent salt, which may be obtained in granular crystals from a solution concentrated to the consistence of a syrup. A small quantity of ammonia throws down from the solution a light yellow subsalt, which when added in excess it redissolves, and leaves silicate of silver.\*\*
- 26. Fluo-silicate of platinum. A yellowish brown salt, very soluble in water. When evaporated to a tough syrup and then digested in water, it leaves a brown coloured subsalt undissolved.++
- 27. Fluo-silicate of antimony. It dissolves readily in water containing an excess of acid. By slow evaporation it crystallizes in prisms, which when dried fall rapidly to powder.‡‡
  - 28. Fluo-silicate of chromium. A green coloured uncrystal-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1823, p. 346.

† Ibid. p. 346.

† Ibid. p. 345.

† Ibid. p. 346.

\*\* Ibid. p. 347.

† Ibid. p. 346.

class v. lizable transparent mass, which deliquesces when exposed to the air.\*

# SECTION IV. --- OF FLUO-MOLYBDATES.

An account of fluo-molybdic acid has been given in p. 200 of this volume. In the same place the reader will find a description and analysis of fluo-molybdate of potash, the only one of the salts of this genus hitherto examined by chemists.

# SECTION V.-FLUO-TUNGSTATES.

The reader will find an account of fluo-tungstic acid, and of fluo-tungstate of ammonia, and fluo-tungstate of potash, the only salts belonging to this class hitherto investigated, in p. 202 of this volume.

#### SECTION VI. -- OF FLUO-CHROMATES.

An account of fluo-chromic acid will be found in p. 204 of this volume. No attempt has hitherto been made to combine it with bases. Hence this genus of salts, supposing it to exist, is still unknown.

#### SECTION VII. -- OF FLUO-COLUMBATES.

An account of fluo-columbic acid will be found in page 205 of this volume. For the only salts of this genus hitherto investigated, we are indebted to Berzelius. They are the following:

- 1. Fluo-columbate of ammonia. This salt resembles the fluo-columbate of potash, but it is much more soluble in water. When redissolved in water it is decomposed, a white powder being precipitated. When sublimed in a platinum vessel, hydro-fluate of ammonia sublimes containing columbic acid. Fluo-columbic acid remains, which is not altered by heat.
- 2. Fluo-columbate of potash. It may be obtained when fluo-columbic acid is saturated with potash till a precipitate begins to fall. The liquid should be hot, otherwise the whole is apt to become solid. On cooling the salt is deposited in scales. They dissolve with difficulty, but completely, in water. Hot water dissolves the salt more easily; but boiling water decomposes it, and occasions the precipitation of a white powder.

Fluo-columbic acid and potash seem capable of uniting in various proportions; in two of which the acid bears the pro-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1823, p. 346.

<sup>†</sup> Ibid. 1824, p. 284.

portion of  $1\frac{1}{2}$  and 2. The salt just described contains the sect. VIII. smallest proportion of acid. When fluoric acid is added to the solution of this salt, it separates one-third of the potash to compose an acid fluoride of potassium. We always obtain the new salt resulting from this operation, when columbic acid is fused with potash, and the mass, after being dissolved in boiling water, is saturated with fluoric acid in excess. It is soluble with difficulty in water, and crystallizes in small needles. These salts are anhydrous, and may be fused and exposed to a white heat in a platinum crucfble without losing their acid. Even when mixed with bisulphate of potash, and exposed to a white heat, nothing is given off but sulphuric acid. \*

- 3. Fluo-columbate of soda. This salt is very soluble in water. It has only been obtained in the form of an irregular saline mass.+
- 4. Fluo-columbate of lime.
  5. Fluo-columbate of magnesia.
  These salts are soluble in water. When evaporated they lose a portion of fluoric acid and deposite a compound little soluble in water.;
- 6. Fluo-columbate of lead. This salt is very little soluble in water. §

# SECTION VIII .-- OF FLUO-TITANIATES.

An account of fluo-titanic acid has been given in page 207 of this volume. For the few salts of this genus hitherto examined we are indebted to Berzelius.

- 1. Fluo-titaniate of ammonia. This salt has a close resemblance to fluo-titaniate of potash; but it is more soluble in water. When distilled it undergoes very remarkable changes. When heated in a platinum vessel at a temperature below redness, hydro-fluate of ammonia sublimes; but it does not At a red heat it fuses and sublimes without alteration, in flocks, without assuming any crystalline shape. This sublimate is soluble in water. Its taste is acid and astringent, The solution of it is capable of dissolving a great deal of alkali before any precipitation takes place. When enough of potash is added to occasion a precipitate, the smell of ammonia becomes intense.
- 2. Fluo-titaniate of potash. Described in p. 207 of this volume.

II.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1824, p. 283. + Ibid. p. 284. ‡ Ibid. p. 285. **∮** Ibid. p. 288. || Ibid. p. 280. 3 ĸ

Class VI.

- 3. Fluo-titaniate of soda. This salt is much more soluble in water than the preceding. It has been obtained only in a saline mass, without regular crystals.\*
- 4. Fluo-titaniate of lime. It is only soluble in water when there is an excess of acid. By evaporation it yields prismatic crystals. When these are dissolved in water an insoluble white powder remains.†
- 5. Fluo-titaniate of magnesia. This salt is very soluble in water. Its taste is bitter. By spontaneous evaporation it yields acicular crystals, which are no longer completely soluble in water.
- 6. Fluo-titaniated peroxide of iron. It forms a yellow liquid, which, by spontaneous evaporation, assumes the form of a yellow limpid syrup. When evaporated by the application of a gentle heat, it yields a crystalline mass, which is decomposed when redissolved in water.
- 7. Fluo-titaniate of lead. It is very soluble in water. By evaporation it is obtained in small colourless crystals, the taste of which is at first sweet; but they leave an impression of bitterness in the mouth. They may be dissolved in water without undergoing decomposition.§
- 8. Fluo-titaniate of copper. This salt is very soluble in water. By spontaneous evaporation, it yields account crystals of a pale bluish green colour, having the same form as the fluo-titaniate of magnesia. The salt is partly decomposed when dissolved in water.

#### CLASS VI.

### CYANOGEN ACID SALTS.

This class of salts will ultimately contain a great number of genera, and in number may not unlikely vie with the oxygen acid salts themselves. It promises also to throw light upon the nature of organic compounds, respecting which at present chemists are not able to form very definite notions. For cyanogen is not only itself derived from the animal kingdom; but it is liable to undergo changes quite analogous to those, which puzzle us so much at present, when we attempt to ob-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1824, p. 280. † Ibid. p. 281. † Ibid. p. 282. † Ibid. p. 282.

tain definite views respecting the organic kingdoms of nature. In the present state of our knowledge only a very imperfect sketch of this class of salts can be presented to the chemical reader.

Sect. I.

# SECTION I. OF CYANODIDES AND HYDRO-CYANATES.

We have the most satisfactory evidence that cyanogen is capable, like chlorine, bromine, iodize, and fluorine, of combining with the different salifiable bases, and of forming with them compounds which in general possess the properties of salts.

1. Hydro-cyanate of ammonia. This salt may be obtained by mixing hydro-cyanic acid with liquid ammonia. By spontaneous evaporation it may be obtained in cubes or rectangular four-sided prisms; but it usually shoots into feather-shaped crystals. Very volatile, boiling at the temperature of 97°. At the temperature of 71°½ the elasticity of its vapour is such that it supports a column of mercury 1.77 inch in length.\* Its smell and taste is a kind of combination of the smell and taste of hydrocyanic acid and ammonia. According to Berzelius, the crystals of this salt are anhydrous. The application of heat very speedily destroys this salt. Its vapour burns with flame, and carbonate of ammonia is formed. The salt is easily soluble in water-and alcohol. Its constituents are

1	atom	hydro-cy	zanic acid	•	•	3.375
I	atom	ammonia	ı .	•	•	$2 \cdot 125$
						<del></del>

2. Cyanodide of potassium. Potassium absorbs very little cyanogen unless it be heated, when an atomic proportion of potassium absorbs an atomic proportion of cyanogen. When potassium is heated in hydro-cyanic acid the same absorption takes place, while the hydrogen gas is set at liberty. But the easiest method of obtaining cyanodide of potassium is to expose common prussiate of potash to a strong heat in a covered platinum crucible and then to dissolve it in water, filter the solution, and evaporate. The cyanodide of potassium is obtained in the state of a fine white salt. By this process, the iron in the salt is deprived of its cyanogen and rendered insoluble. That the white salt thus obtained is a cyanodide of potassium is obvious from this: If you dissolve it in water and put a plate of copper into the liquid, potassium is disengaged.

Class VI. This salt is very white; its taste is bitter and alkaline. It is said to smell of hydro-cyanic acid; but I have obtained it destitute of smell altogether. It dissolves readily in water and alcohol. The dry salt contains no water of crystallization, but is a compound of

l atom cyanogen l atom potassium	•	•	3·25 5
•			
			9.05

- 3. Cyanodide of sodium. This salt may be formed by dissolving soda in liquid hydro-cyanic acid, or by decomposing a solution of hydro-cyanate of lime by means of carbonate of soda. By evaporating the filtered solution the cyanodide of sodium is obtained in the state of a white salt. It resembles the preceding salt very closely in its properties; but has not been hitherto subjected to a rigid analysis. Doubtless it might be prepared in the same way as the cyanodide of potassium.

  4. Cyanodide of barium. When hydro-cyanic acid is added
- to barytes water till the liquid ceases to precipitate muriate of magnesia, this salt is formed. It is exceedingly easily decomposed. When boiled, carbonate of ammonia is disengaged, and carbonate of barytes falls down. When alcohol is mixed with the liquid in sufficient quantity, the cyanodide of barium falls down in silky transparent needles. When dissolved in water, if we evaporate the solution, the salt is decomposed, tercarburet of azote\* and carbonate of barytes being formed.
- 5. Cyanodide of calcium. This salt, as Wöhler has shown, may be obtained by passing the vapour disengaged when urate of mercury is heated, through lime water. It does not crys-When hydrate of lime is dissolved in an aqueous solution of hydro-cyanic acid the same salt is formed. When the liquid is heated the salt is decomposed into carbonate of ammonia and carbonate of lime.
- 6. Cyanodide of magnesium. Hydrated magnesia dissolves readily in liquid hydro-cyanic acid. Heat decomposes the salt in the same way as the preceding. I am not aware that any attempt has been made to obtain anhydrous cyanodide of magnesium.
- 7. Cyanodide of aluminum. Scheele has shown that hydrocyanic acid is not capable of dissolving hydrated alumina.

<sup>\*</sup> I give this name to the dark brown substance described in Vol. I. p. 211, of this work.

However, it appears from the experiments of Ittner, that hydro-cyanic acid and alumina may be combined by double decomposition.

Sect. 1.

8. Cyanodide of iron. This salt was obtained by Berzelius by heating prussiate of ammonia in close vessels till all the hydro-cyanate of ammonia was disengaged. It is a grayish yellow matter, which may be preserved undecomposed. When exposed to a stronger heat it becomes brown, giving out azotic gas. When still farther heated it becomes black bicarburet of iron. At a red heat it takes fire and burns like tinder, leaving peroxide of iron, which weighs just as much as the bicarburet.\*

It is believed at present, that there exists also a sesquicyanodide of iron analogous to peroxide and perchloride of iron, but it has not yet been obtained except in combination.

- 9. Cyanodide of manganese. It is precipitated when a solution of cyanodide of potassium is mixed with a protosalt of manganese. The stronger acids decompose it. Water does not dissolve it, but it is soluble in the alkaline prussiates.
- 10. Cyanodide of nickel. Hydro-cyanic acid precipitates acetate of nickel completely, and sulphate and nitrate of nickel partially. The precipitate is light apple green, but when dried it becomes leek green. When heated it gives out water, and a light brown matter remains, which is a cyanodide of nickel. When strongly heated it gives out cyanogen and azotic gas, and leaves a mixture of metallic nickel and charcoal.†
- 11. Cyanodide of cobalt. According to Scheele, carbonate of cobalt dissolves with effervescence in liquid hydro-cyanic acid. The salt precipitates when solutions of cyanodide of potassium and a cobalt salt are mixed together. It is a brownish white powder, insoluble in water and in acids.

* Bicarburet of in	ron is a compound	l of		•
	2 atoms carbon			1.5
	l atom iron		•	3.2
Peroxide of iron of				5
Peroxide of Iron of				
	1½ atom oxygen	•	•	1.2
	l atom iron	•	•	3.2
				5
				Ü

Hence the reason why the weight continues unaltered. + Wöhler.

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- 12. Cyanodide of zinc. According to Scheele, when hydrocyanate of lime is mixed with sulphate of zinc a white precipitate falls, neither soluble in water nor in an excess of hydrocyanate of lime. But the stronger acids dissolve it while hydrocyanic acid is disengaged. When this salt is distilled carbonate of zinc remains behind.\*
- 13. Cyanodide of lead. When acetate of lead and cyanodide of potassium are mixed a white heavy precipitate falls, which is not soluble in water, but dissolves in the stronger acids with the evolution of hydro-cyanic acid.
- 14. Cyanodide of tin. This salt has not yet been examined. It has been ascertained that none of the salts of tin are precipitated by cyanodide of potassium.
- 15. Cyanodide of copper. Aqueous hydro-cyanic acid when digested over copper with the assistance of heat, occasions an effervescence, and forms a brownish yellow matter. Cyanodide of potassium or calcium when not added in excess throw down from all the solutions of oxide of copper a similar precipitate. The salt, if left in the liquid, undergoes decomposition, while cyanogen is evolved.
- 16. Dicyanodide of copper. When hydro-cyanic acid, or cyanodide of potassium, is mixed with dichloride of copper a white cheesy precipitate falls. When this precipitate is gently heated it melts into a brownish matter. If the heat be continued there comes over first a liquid which reddens litmus paper, then ammonia is disengaged, and a brownish residue remains behind. The salt dissolves in liquid ammonia into a colourless solution, in concentrated muriatic acid it dissolves with a yellow colour.
- 17. Cyanodide of mercury. This salt in a crystallized state seems to have been first obtained by Berthollet, but it was Gay-Lussac that first pointed out its real nature. It is easily obtained by digesting a mixture of red oxide of mercury and prussian blue in a sufficient quantity of water. If the two substances be used in the requisite proportions, the prussian blue loses its blue colour, and the oxide of mercury dissolves. When the filtered solution is concentrated the cyanodide of mercury is deposited in large white translucent crystals. The primary form of these crystals is a right square prism. The base of the prism is frequently replaced by two faces, rising from two opposite angles of the prism and meeting at an angle

of 114°.\* It has a bitter, and, at the same time, a mercurial and very disagreeable taste. It dissolves readily in water and in weak alcohol. Its constituents, as determined by the analysis of Gay-Lussac, are

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1 atom cyanogen		•	3.25
l atom mercury	•	•	12.5
			15.75

When heated it blackens, gives out cyanogen gas, while mercury is disengaged. There is formed at the same time a very light black charry matter, which Mr. Johnston assures us is composed of the very same constituents as cyanogen, namely, I atom azote, and 2 atoms carbon; but the properties of the substance are scarcely compatible with that opinion. It has been generally considered as a compound of I atom azote, and 3 atoms carbon; but I am not aware that these constituents have been established by satisfactory experiments. When this salt is distilled while moist, there are disengaged carbonic acid, ammonia, hydrocyanic acid, and mercury. When mixed with sulphuric acid, it forms a gelatinous mass, having a weak odour of hydro-cyanic acid. When there is an excess of sulphuric acid, it becomes yellow, while hydro-cyanic acid is disengaged.

This salt is not decomposed by aqueous solutions of the oxygen acids, not even by nitric acid, nor by the aqueous solutions of alkalies.

18. Subcyanodide of mercury. This compound was obtained by Grouvelle, who boiled a solution of cyanodide of mercury on red oxide of mercury, till the liquid refused to take up any more. From the quantity dissolved, he has drawn as a conclusion, that the new compound is formed of

3 atoms cyanodide of mercury . 47.25 2 atoms red oxide of mercury . 27

**74**·25†

When the solution is evaporated, it yields small, four-sided, oblique needles.

19. Cyanodide of silver. It is obtained when nitrate of silver is mixed with hydro-cyanic acid, or cyanodide of potassium. It constitutes a white curdy precipitate. When heated in a

<sup>\*</sup> Brooke, Annals of Philosophy (2d series), vi. 42.

<sup>†</sup> Ann. de Chim. et de Phys. xvii. 54.

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close vessel, it gives out a portion of cyanogen, and melts into a mass, which has a reddish brown colour while hot, but becomes gray when cold. When heated in the open air, the whole cyanogen is disengaged.

- 20. Cyanodide of gold. Hydro-cyanate of lime or potash throws down muriate of gold white. When heated, the salt becomes yellow. When heated still more strongly, water and gaseous matter are given off, and there remains a mixture of gold and charcoal. This salt is soluble in liquid ammonia.
- 21. Cyanodide of platinum. Hydro-cyanic acid has no action on oxide of platinum, and hydro-cyanate of lime does not produce a precipitate in the solutions of platinum.\*
- 22. Cyanodide of palladium. A light yellow white powder. When prepared from nitrate of palladium, it detonates like gun-powder, with a weak light, as Wollaston ascertained.

# SECTION II. -- OF CYANATES.+

To the acid described in page 225 of this volume under the name of cyanous acid, Wöhler, who discovered it, gave at first the name of cyanic acid. This name was changed into cyanous acid, in consequence of the discovery, by Serullas, of another acid, which he considered as cyanogen combined with twice as much oxygen as exists in Wöhler's acid. But it has been since ascertained by Wöhler and Liebig, that the acid of Serullas contains also hydrogen. Hence its constitution is quite different from that of Wöhler's acid. It will be expedient, in consequence of this discovery, to restore the name cyanic to the acid of Wöhler, and to distinguish the acid of Serullas by a new appellation.

1. Cyanate of potash. I have given the process for obtaining this salt in page 226 of this volume. It is composed of small plates or needles, and has some resemblance to chlorate of potash. It has the taste of saltpetre, is not altered by exposure to the air, and in a red heat it fuses and is decomposed. When the solution of it in water is boiled, the salt is completely changed into carbonate of potash, while ammonia is disengaged. The same change takes place gradually even without the application of heat. When hydrogen gas is passed

<sup>\*</sup> Scheele.

<sup>†</sup> This acid and its salts ought to find its place among the oxygen acids and their salts. But I have placed them here provisionally, because I consider many points respecting the compounds of cyanogen as not yet fully established.

Sect, 11.

over the ignited salt, it deprives both of its constituents of their oxygen, and a cyanodide of potassium is formed. But the water produced by this decomposition, decomposes another portion of the salt into carbonate of potash and ammonia. Potassium dissolves in this salt with tranquillity. The solution consists of a mixture of cyanodide of potassium and potash. Iron filings heated to redness in it, form cyanodide of potassium, ferro-cyanodide of potassiam, and protoxide of iron. When sulphur is melted with it, the products are sulphocyanodide of potassium, sulphufet of potassium, and sulphate Sulphuretted hydrogen gas changes the fused salt into a yellow mass of sulphuret of potassium, and sulpho-cyanodide of potassium, while at the same time some hydro-sulphuret of ammonia sublimes in consequence of the water formed during the action. When heated with concentrated sulphuric acid, carbonic acid is evolved, and sulphates of potash and of ammonia are formed. Diluted sulphuric acid causes the evolution of some cyanic acid, which escapes with the carbonic acid. This salt is readily dissolved in water. soluble in hot alcohol of the specific gravity 0.832, but not in absolute alcohol. Its constituents, according to the analysis of Wöhler, are

1 atom cyanic acid	•	•	4.25
1 atom potash	•	•	6
			10.25

- 2. Cyanate of soda. This salt, according to Wöhler, is capable of crystallizing.
- 3. Cyanate of barytes. The method of forming this salt has been described in page 225 of this volume. It crystallizes in transparent silky needles. When ignited with sulphur, there are formed hydro-sulphuret of ammonia, sulphate of barytes, sulphuret of barium, and sulpho-cyanodide of barium. When this salt is dissolved in water, and the solution evaporated, it is decomposed into carbonate of barytes, and tercarburet of azote.\*
- 4. Cyanate of lime. It may be prepared by the same process as the preceding salt, by passing the vapour from heated urate of mercury through lime water. It does not crystallize.+
  - 5. Cyanate of iron. This salt may be obtained by decom-

Class VI.

posing cyanate of silver by means of iron. The solution is very easily decomposed.

6. Cyanate of lead. When solutions of acetate of lead and cyanate of potash are mixed together, a white heavy precipitate falls in fine needles, and resembling chloride of lead. It is anhydrous, and, according to Wöhler, is a compound of

Cyanic acid		•	•	23
Oxide of lead	'n,	•	•	77
	Ç			100

This is obviously

1 atom cyanic acid	•	•	4.25
1 atom oxide of lead	•	•	14
			18.95

When heated in a close vessel, it melts, becomes red, and is at last changed into a light green powder, which seems to be a mixture of lead and cyanodide of lead. When heated in contact with air, it burns, and is easily reduced to metallic lead, with the emission of sparks. Potash disengages cyanic acid, while a reddish yellow crystalline powder precipitates. Sulphuretted hydrogen produces sulphuret of lead, while cyanic acid is disengaged; but in consequence, probably, of the water formed, it is soon decomposed into carbonic acid and This salt is slightly soluble in boiling water.\*

- 7. Cyanate of copper. When cyanate of lime is dropt into nitrate of copper, a greenish brown precipitate falls.†
- 8. Cyanated suboxide of mercury. Cyanate of barytes, when mixed with a solution of nitrated suboxide of mercury, occasions a white precipitate, which, when heated, gives out sometimes cyanic acid, and sometimes carbonic acid and azotic gas. A porous charry matter remains, from which acids are capable of extracting potash.
- 9. Cyanate of silver. Obtained by mixing nitrate of silver and cyanate of potash together. It is a white powder, which after being dried contains no water; but, as is obvious from the analysis of Wöhler and Liebig, is composed of

1 atom cyanic acid . 1 atom oxide of silver	•	4·25 14·75
		19

<sup>\*</sup> Wöhler. † Ibid. ‡ Ibid.

<sup>§</sup> Ann. de Chim. et de Phys. xxxiii. 209.

Sect. III.

When heated in the open air, vapour of cyanic acid is given out, together with a mixture of two volumes carbonic acid, and one volume azotic gas. When ignited, it becomes black, melts, takes fire, and burns with noise. When ignited in close · vessels, it leaves cyanodide of silver. When this mass is further heated in the open air, much cyanogen is driven off, and 49 per cent. of silver remains. - When heated with acids, cyanic acid is given off, together with carbonic acid, while silver and ammonia remain in the acid solution. It absorbs muriatic acid gas, while heat is evolved; chloride of silver is formed, and aqueous cyanic acid disengaged, constituting a thick solution, which, by a gentle heat, is converted into bicarbonate of ammonia, speedily changed into sal ammoniac by an additional dose of muriatic acid gas. From the solution of this salt in water, iron throws down metallic silver. Cyanate of silver is slightly soluble in boiling water, but not in cold water. When the solution cools, it again falls down in powder. It is readily soluble in liquid ammonia.\*

#### SECTION III. -- OF CYANURATES.

The acid discovered by Serullas in 1829, and described in page 227 of this volume, under the name of cyanic acid, has been lately examined anew by MM. Wöhler and Liebig, who have detected in it hydrogen, and have shown that it is in fact a compound of

• 0			
1 atom hydrogen	•	•	0.125
2 atoms oxygen	•	•	2.00
l atom cyanogen	•	•	3.25

This analysis differs from that of Serullas, simply by the addition of an atom of hydrogen, which, in consequence of the smallness of its weight, had been at first overlooked. In consequence of this difference in the nature of this acid from the cyanic acid of Wöhler, the name of cyanuric acid; has been applied to it by Wöhler and Liebig.

The salts which this acid forms with bases, will receive, of course, the name *cyanurates*. Serullas informs us, that they are well characterized by their crystalline forms, and by their

<sup>\*</sup> Wöhler. † Ann. de Chim. et de Phys. xlvi. 37.

<sup>‡</sup> From cyanogen and urca, to show its intimate connexion with these two important principles.

interesting chemical properties.\* But hitherto none of them have been described, or accurately examined.

# SECTION IV .- OF FULMINATES.

The first knowledge of the fulminates was the consequence of the well known experiments of Howard, who made known the fulminates of mercury and silver about the beginning of the present century. It was Liebig who first showed that they owe their properties to a peculiar acid, to which he gave the name of fulminic. He showed that this acid may be combined with the different bases, and that all the salts so formed, possess the property of fulminating, when heated. He gave the most complete examination of the fulminates yet made, we are indebted to Mr. Edmund Davy, who published a very interesting paper on the subject, in the Transactions of the Royal Dublin Society.

- 1. Fulminate of ammonia. Mr. Davy obtained this salt by adding sulphate of ammonia to a solution of fulminate of barytes, as long as a precipitate continued to fall. The filtered solution was colourless, but when evaporated nearly to dryness, at the common temperature of the air, it assumed a yellow colour, and was of a thick syrupy consistence. It had a sweet and astringent taste. By a gentle heat it becomes tough and then brittle. It explodes in this state by percussion and by heat, producing a sharp report and a yellowish flame. 'It is deliquescent and soluble in water, forming a yellow solution which tinges turmeric paper, and has a sweet taste with a considerable degree of astringency. Its fulminating properties are not altered by exposing the salt to air and moisture.‡
- 2. Fulminate of potash. Mr. Davy obtained this salt by the same process as the preceding, only substituting sulphate of potash for sulphate of ammonia. The colourless liquid thus got was slightly alkaline; but Liebig informs us, that he got the salt perfectly neutral. When slowly evaporated it crystallizes in small right rhombic prisms. Colour at first white, but it becomes yellow when the salt is dried in an artificial heat. The crystals have a sweet taste, and are deliquescent. They dissolve readily in water, but not in alcohol. When heated, they explode with a loud report, and a faint reddish flame. When dry, the salt fulminates by percussion, friction,

<sup>\*</sup> Ann. de Chim. et de Phys. xxxviii. 384.

<sup>+</sup> Ibid. xxiv. 314.

<sup>‡</sup> E. Davy, p. 40.

<sup>§</sup> Ann. de Chim. et de Phys. xxiv. 315.

and the contact of strong sulphuric acid. The fulminating Sect. 1V. property is not impaired by exposure to the atmosphere.\*

According to the analysis of Liebig, the constituents of this fulminate are

Fulminic acid 85.08 Potash 14 92

100.00+.

This is equivalent to

8 atoms fulfinic acid,

1 atom potash

if we adopt 4.25 as the atomic weight of the acid. If the atomic weight be 5.25, then the acid present amounts to about 6 atoms.

3. Fulminate of soda. Mr. Davy obtained this salt by a process similar to that which furnished the preceding. When the filtered solution is evaporated, the salt is obtained in oblique rhombic prisms with dihedral summits, and in very long white needles, at first transparent, but becoming opaque by the loss of water. These crystals have a sweet and astringent taste, and effloresce when exposed to the air. This salt has a close resemblance to fulminate of potash, but its specific gravity is Its constituents, according to Liebig, are less.

•	Fulminic acid	•	•	88.66
•	Soda	•	•	11.34

100.001

This is equivalent to six atoms acid and one soda, provided the atomic weight of the acid be 5.25.

4. Fulminate of barytes. Mr. Davy obtained this salt by adding about three volumes of aqueous solution of fulminate of zinc, to one volume of a saturated aqueous solution of barytes. oxide of zinc precipitates, and the filtered liquid is a solution of fulminate of barytes. It has a sweetish astringent taste, and when evaporated to a syrup, it crystallizes in small prisms intersecting each other. These crystals, by exposure to the air, acquire a yellow colour. The lustre of the crystals is vitreous; they dissolve in water and in alcohol. They change turmeric paper to brown. When heated, this salt explodes powerfully, producing a yellow flame. It explodes also by percussion, friction, and the action of strong sulphuric acid.

<sup>\*</sup> E. Davy, p. 38.

<sup>+</sup> Ann. de Chim. et de Phys. xxiv. 316.

<sup>†</sup> Liebig, ubi supra.

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Its dilute solution is decomposed by the more powerful acids, fulminic acid being evolved. When exposed to the air it undergoes no other change than a slight alteration in colour. When mixed in a dry state with pulverized flints, and distilled in a small retort, there came over carbonate of ammonia in crystals, water, carbonic acid, and azotic gas.\*

Liebig is of opinion that fulfininic acid and barytes combine

in two different proportions. b

- same process as the preceding, substituting strontian water for barytes water. It forms transparent white crystals, having a glassy lustre. They are excessively small. When slightly heated they become yellow. The taste is sweet and astringent. The salt is soluble in water. It changes turmeric paper to brown. It fulminates strongly when heated, producing a feeble yellow flame. It explodes also by percussion, friction, and by the contact of strong sulphuric acid. When exposed to the air it becomes moist, and then does not explode by the acid.
- 6. Fulminate of lime. It was obtained by adding lime water in slight excess to fulminate of zinc, and filtrating. It has a sweetish and bitter taste, and yields crystals so small that the shape cannot be determined. The colour is at first white, but it becomes yellow when gently heated. It absorbs moisture from the air. It is slightly soluble in water. The dry salt explodes by percussion, friction, and heat, producing a loud report, and a reddish coloured flame, with a tinge of yellow.
- 7. Fulminate of magnesia. This salt may be obtained by adding sulphate of magnesia to a solution of fulminate of barytes, as long as a precipitate continues to fall. The filtered solution is colourless, and has a sweet and astringent taste. By the requisite concentration, it yields crystals in long flat four-sided opaque prisms, intersecting each other in different directions. The salt neither alters litmus nor turmeric paper. It is soluble in water, but scarcely so in alcohol. When dry, it explodes by friction, percussion, and heat, producing a loud report, and a reddish coloured flame. But it does not explode by strong sulphuric acid, even when artificially heated.

According to Liebig there is another fulminate of magnesia, which is an insoluble rose red powder that does not fulminate but merely decrepitates.

<sup>\*</sup> E. Davy, p. 34. † Ibid. p. 36. ‡ Ibid. p. 37. § Ibid. || Ann. de Chim. et de Phys. xxiv. 315.

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- 8. Fulminate of alumina. It was obtained by treating a solution of fulminate of barytes with neutral sulphate of alumina, as long as a precipitate continued to fall. The filtered liquid, when evaporated to dryness, leaves a yellow, imperfectly crystallized substance, which is fulminate of alumina. It explodes feebly by percussion and heat, producing a yellow flame. Its taste is astringent, with a slight impression of sweetness. It is soluble in water, forming a yellow fluid, which does not alter vegetable colours.\*
  - 9. Fulminate of iron. Mr. Davy prepared this salt by putting nearly equal bulks of Howard's fulminating powder and iron filings, in a small ground stoppered bottle, which was then filled with water, closed, and occasionally agitated. In a short time the decomposition of the fulminate of mercury began, the filings were tarnished, and the liquid acquired a yellowish tint, which gradually became deeper. In about an hour or two all the fulminate of mercury was decomposed, and the fulminate of iron formed.

The filtered liquid has a dull yellow colour, a peculiar astringent taste, and slightly reddens litmus paper. Dilute acids gave the liquid a fine red colour, which disappears after some hours, while a peculiar odour of fulminic and hydro-cyanic acid is perceptible. Dilute muriatic acid strikes a similar colour, which gradually becomes deeper than port wine, while the smell of hydro-cyanic acid becomes perceptible.

When the solution of this fulminate is evaporated, it becomes first the colour of port wine, then bluish black, while a little blackish precipitate falls which has no fulminating properties. When evaporated to dryness, it leaves a similar substance, which becomes brownish black after ignition. From these and many similar experiments by Mr. E. Davy, it is obvious that this fulminate is very liable to undergo spontaneous decomposition, and that it cannot be obtained in a dry state without the destruction of its acid.+

10. Fulminate of manganese. It may be obtained by adding sulphate of manganese to a solution of fulminate of barytes as long as a precipitate continues to fall. The filtered solution is colourless. When evaporated to the consistence of a syrup it has a sweet taste with a certain degree of astringency. By continuing the evaporation, a tenacious mass is obtained which explodes by percussion and heat, producing a reddish flame.

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It is a neutral salt which is soluble in water. Dilute sulphuric acid decomposes the salt, fulminic acid being evolved.\*

11. Fulminate of nickel. It may be obtained by mixing nickel filings and fulminate of mercury in a phial, in the way described when treating of the preparation of fulminate of iron. In a few days the water in the phial acquires a green colour. The filtered liquid, when evaporated, leaves a crust of a yellowish green substance, which explodes by heat, producing a sharp noise, and an enlarged flame.

It dissolves in pure ammonia, and the solution, when evaporated, leaves a pale yellowish green substance, which seems to be a double salt, composed of fulminic acid, oxide of nickel, and ammonia. When heated, it is decomposed with a hissing noise, and successive flashes of light.

A fulminate of nickel, different from the preceding, is obtained by adding sulphate of nickel to fulminate of barytes, as long as any precipitate falls, and then filtering. The liquid has a yellow colour, and when evaporated, leaves a yellow crust with some very minute crystals. The colour of this fulminate is straw yellow. It explodes by percussion, and more strongly by heat, producing occasionally small red flashes of light, and a large red flame. It is soluble in water.†

- 12. Fulminate of cobalt. It may be obtained by adding sulphate of cobalt to fulminate of barytes, as long as a precipitate falls, and then filtering. A yellow liquid is obtained which yields yellow crystals in groups, having the form of long rhomboidal prisms. They are insoluble in cold, but slightly soluble in boiling water, and in liquid ammonia. This salt explodes by friction, percussion, and heat, producing a loud report, and a large reddish flame. It does not explode by means of strong sulphuric acid, even after being dried. When mixed with pulverized borax, and heated, it is decomposed, and by increasing the heat, a deep blue glass is obtained.
- 13. White fulminate of zinc. This salt may be obtained by mixing about equal parts of zinc filings and fulminate of mercury in a small phial filled with water and closed by a glass stopper. The mixture is occasionally agitated for about fifteen minutes. Heat is produced, the fulminate of mercury is gradually decomposed, running mercury being precipitated and zinc dissolved in its place. The liquid is colourless, and has

<sup>\*</sup> E. Davy, p. 41.

<sup>†</sup> Ibid. p. 45.

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a sweet and astringent taste. By spontaneous evaporation it deposites white crystals in small rhomboidal tables. When a plate of zinc is plunged into a solution of fulminate of barytes, a little fulminate of zinc is precipitated in white powder, but it is impure. Solid white fulminate of zinc is tasteless, and insoluble in water. When heated to 350° it explodes, producing a sharp report and a red flame. It also explodes when struck on an anvil with a hardmer, and likewise by friction when mixed with a little powdered sand. When a drop of sulphuric acid is brought in contact with a lump of fulminate of zinc it explodes loudly with a red flame. When a little of it is thrown into sulphuric acid it is decomposed with the evolution of gas. The same decomposition is produced by muriatic, nitric, and phosphoric acids. The salt dissolves in solutions of potash and soda, and a peculiar smell is perceptible, not unlike that of boiled lobster or crawfish. Ammonia also dissolves it.

When aqueous fulminate of zinc is poured into a bottle of chlorine gas a yellow oily fluid is produced, not unlike chloride of azote, but destitute of its explosive properties. This liquid is volatile, has an acrid and peculiar smell, a sweet and astringent taste, with a certain degree of pungency, which remains for sometime in the mouth. It is insoluble in water, but forms a saponaceous compound with ammonia. It does not immediately redden litmus paper, but acquires that property after some time.\*

14. Yellow fulminate of zinc. This salt is obtained by exposing the colourless aqueous solution of the preceding salt when first formed to evaporation at a moderate heat on the sand bath. As the process proceeds small globules of gas appear to be disengaged from the fluid, which first assumes a yellow tint, then grows darker, and there ultimately remains a brittle yellow crust, which constitutes yellow fulminate of zinc. It forms minute crystals, the shape of which cannot be determined. It is insoluble in cold, and slightly soluble in boiling water. It is also insoluble in alcohol, but it dissolves readily in aqueous ammonia. It is decomposed by the strong acids like the preceding salt, but it does not explode with sulphuric acid. It explodes by percussion, and likewse by friction while warm. It explodes also when heated to 350°, but not with such violence as the white fulminate. When this salt,

Class VI.

previously dried at the temperature of 230°, is mixed with pulverized fint and distilled, the fulminic acid is decomposed, and the products are water, carbonic acid, azotic gas, and crystallized carbonate of ammonia.\*

- 15. Fulminate of cadmium. This salt may be obtained by adding sulphate of cadmium to fulminate of barytes as long as a precipitate falls, and then Atering the solution. By evaporation a number of very small opaque white crystals are formed, grouped together in prisms diverging from a common centre. This fulminate acquires a yellowish tint when dried on the sand bath, or by exposure to the air for a few days. It is soluble in water, and explodes by percussion and heat, producing a sharp report and a feeble yellowish flame.
- 16. Fulminate of lead. This salt may be obtained by adding a solution of nitrate of lead to a solution of fulminate of barytes, or solutions of fulminate of zinc and nitrate of lead mixed together may be heated. A white powder falls, which under the microscope appears to consist of crystalline scales. When heated it explodes violently, and at the same time a large whitish flame appears. It also explodes by percussion and friction. Sulphuric acid decomposes it, as does also nitric acid.‡
- 17. Fulminate of copper. Mr. Davy obtained this salt in three states, namely, brown, green, and white.
- (1.) When copper filings, fulminate of mercury, and water, are put into a closed phial, and the whole occasionally agitated, decomposition takes place. Metallic mercury is precipitated in flocks, and a brown matter is formed, which is brown fulminating copper. The liquid and mercury are easily separated by decantation, and the brown powder being washed may be collected on a filter, and dried in a heat not exceeding 212°. It is a very formidable substance, and should be handled with great caution. It explodes with great violence when heated to 400°, and also by percussion and friction. This fulminate is formed when an aqueous solution of fulminate of zinc is placed on a clean copper plate and heated or evaporated to dryness. It is formed also when copper filings are put in a glass plate moistened with water, and placed over a wine glass which contains a solution of fulminate of barytes mixed with dilute sulphuric acid.

<sup>\*</sup> E. Davy, p. 32. † Ibid. p. 45.

- (2.) When the liquid, after having deposited the brown sect. IV. fulminate of copper, is filtered, and evaporated by a gentle heat, the green fulminate of copper is deposited in minute crystals, consisting of flat pyramidal dodecahedrons. It has a light green colour, and an astringent taste. When heated on a slip of paper it explodes, producing a large whitish flame, and a much louder report than Allminating mercury.
- (3.) When copper leaf in a minute state of division, fulminating mercury, and distilled water, are put into a small phial with a ground stopper, and the whole occasionally agitated, a gradual change of colour takes place, both in the copper leaf and the fulminating mercury. In about a month small white shining crystals are deposited, consisting of pyramidal octahedrons and rectangular four-sided prisms. When heated on a slip of paper they explode with a loud and sharp report, accompanied by a green flame. They explode also by percussion and friction, and when heated, they explode likewise when in contact with sulphuric acid.\*

18. Fulminate of mercury. This is the salt originally discovered by Mr. Howard, whose process for preparing it is as follows: Dissolve by means of heat 100 grains of mercury in a measured ounce and a half of nitric acid, of the specific gravity of about 1.3. Pour this solution upon two measured ounces of alcohol, and apply heat till the mixture begins to effervesce. The fulminate of mercury gradually precipitates. It is to be washed and dried in a low heat.

It is very little soluble in cold, but more soluble in boiling water. Mr. E. Davy has observed that when exposed to a certain temperature for a little time it undergoes a partial decomposition, by which it loses its white colour and its explosive properties. When recently made it explodes in dry chlorine gas with a large white flame and the production of a white cloud. Its constituents, according to the analysis of Mr. Davy, are as follows:

> 1 atom fulminic acid 5.251 atom oxide of mercury . 13.5 18.75+

19. Difulminate of mercury. When a weak solution of nitrated suboxide of mercury is added to liquid fulminate of zinc, a dark iron gray precipitate falls, which is the substance

Class V1.

in question. After being washed and dried, it explodes by percussion, but more feebly than the preceding salt. It does not explode by strong sulphuric acid. When heated on a slip of platinum, it goes off somewhat like gun-powder, producing a flash of white light. In chlorine gas it is decomposed with a feeble explosion, and a white cloud and flame are produced.\*

20. Fulminate of silver. This is the salt originally prepared by Howard, by the same process as that by which fulminating mercury was obtained. Brugnatelli's process is very easy. He puts into a beer glass 100 grains of dry nitrate of silver, and pours over it one ounce of alcohol, and as much smoking nitric acid. An effervescence takes place, and fulminating silver formed.† Liebig's process is to dissolve 1 part of silver in 20 parts of nitric acid of the specific gravity 1.367, and to pour over the solution 26 parts of alcohol of the specific gravity 0.84. The mixture being raised to the boiling temperature, and kept in that state till a muddiness begins to appear, it is then taken from the fire, and to moderate the boiling, 26 parts of alcohol are added by small quantities at a time.

Fulminating silver is deposited in small, white, opaque needles. When taken internally, it acts as a virulent poison. It does not act on litmus paper. It is anhydrous, or contains only traces of water. When exposed to the light, it becomes black, and is decomposed, carbonic acid, azotic gas, and vapour of water being given out. When heated, it explodes with great violence. It explodes also by percussion and friction, and the contact of concentrated sulphuric acid. When put into dry chlorine gas, it explodes with flame, and a loud report. 36 parts of boiling water dissolve one part of fulminate of silver, but it is again precipitated when the liquid cools. It dissolves easily and completely in liquid ammonia.

We have two analyses of this salt which so far agree, that they show the salt to be a compound of an atom of acid, and an atom of oxide of silver, though they are inconsistent with each other as far as the elements of the acid are concerned. Mr. Edmund Davy found the salt composed of

1 atom fulminic acid . 5.25
1 atom oxide of silver . 14.75
201

<sup>\*</sup> E. Davy, p. 52. ‡ E. Davy, p. 18.

<sup>+</sup> Nicholson's Jour. vii. 285.

According to the analysis of Gay-Lussac and Liebig, the constituents are

I have already pointed out the difference in the constitution of fulminic acid to which these two analyses lead.

21. Fulminate of gold. Wiffen a weak solution of chloride of gold is added to liquid fulminate of barytes, a dark precipitate slowly separates. When washed and dried on the filter, it has a chocolate brown colour, and explodes with a loud report, and a reddish flame, by heat or percussion. It is soluble in dilute muriatic acid. Nitric acid decomposes it.

When the liquid from which the preceding fulminate has precipitated is evaporated after filtration, it yields small yellow crystals in six-sided prisms, which explode by heat and percussion with a reddish and yellowish flame. Whether these crystals be the same as the chocolate powder, or whether they constitute a different species, has not been ascertained.

- 22. Fulminate of platinum. It may be obtained by adding a solution of sulphate of platinum to liquid fulminate of barytes as long as a precipitate falls. A dark brown substance gradually separates, which when washed and dried is fulminate of platinum. When heated, it is decomposed with a hissing noise; by percussion, it is decomposed, producing smoke, but scarcely any sensible noise. This substance consists chiefly of sulphate of barytes. But the liquid from which it separates when evaporated, deposites pure fulminate of platinum in minute rhombic prisms, having a yellowish brown colour, and exploding loudly by heat and percussion.§
- 23. Fulminate of palladium. Nitrate of palladium being added to fulminate of barytes, a dark brown substance gradually falls, which after being washed and dried, explodes by heat with a reddish flame. This fulminate has a dark brown colour, and is tasteless and insoluble in water.
- 24. Fulminate of chromium. This compound may be formed by treating fulminate of barytes with sulphate of chromium. The filtered solution after evaporation yields minute crystals

<sup>\*</sup> Ann. de Chim. et de Phys. xxv. 285.

<sup>†</sup> See page 232 of this volume.

<sup>‡</sup> E. Davy, p. 48. § Ibid. p. 50. || Ibid. p. 51.

Chase VI. of fulminate of chromium, having a yellowish green colour. They are soluble in water, and the solution has a sweet and slightly astringent taste. They explode by percussion 'and heat, producing a feeble report, and a reddish flame.\*

SECTION V.—OF SULPHO-CYANODIDES AND HYDRO-SULPHO-CYAMATES.

From the account of hydro-sulpho-cyanic acid, given in page 241 of this volume, it appears to have for its base a compound of

2 atoms sulphur . . . 4
1 atom cyanogen . . 3.25

To which the name of sulpho-cyanogen has been given. This base, united to one atom hydrogen, constitutes the hydro-sulpho-cyanic acid, or the sulphuretted chyazic acid of Porrett. Most of the saline compounds, into which this acid enters, would appear to be compounds of sulpho-cyanogen and the respective bases; but as the subject has not yet been sufficiently cleared up, I have prefixed both names to this section; though I am of opinion that most of the salts (except the first) are in fact sulpho-cyanodides.

- 1. Hydro-sulpho-cyanate of ammonia. Liquid ammonia dissolves very little hydro-sulpho-cyanic acid. When the solution is evaporated the whole of the ammonia is disengaged.† This salt does not crystallize, but is soluble in alcohol.‡
- 2. Sulpho-cyanodide of potassium. This salt may be obtained by mixing together equal weights of flowers of sulphur and common prussiate of potash, previously deprived of its water and reduced to the state of a fine powder, and fusing the mixture over a spirit-lamp at a temperature a little below ignition. When the fused mass has become cold dissolve it in water and drop into the solution caustic potash till all the oxide of iron is thrown down, then filter and evaporate to dryness. The dry salt thus obtained (if too much potash has not been added) is sulpho-cyanodide of potassium. It crystallizes in long colourless channeled prisms, and needles terminated by four-sided prisms. Its taste is biting, and similar to that of radishes, but it leaves a saline and cooling impression in the mouth. It is poisonous, and acts as a narcotic. When heated

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it melts into a transparent liquid, which assumes a crystalline texture on cooling. If air be excluded, it may be ignited without decomposition; but in an open vessel it is gradually converted into sulphate of potash. According to Porret, it is deliquescent, and I have found it so in my laboratory. It is readily soluble in alcohol. Its constituents, according to the analysis of Berzelius, are

1 atom sulpho-cyanogen 1 atom potassium 12.25

- 3. Sulpho-cyanodide of sodium. This salt crystallizes in rhomboids. It is deliquescent, and soluble in alcohol.\*
- 4. Sulpho-cyanodide of barium. A deliquescent salt, crystallizing in long slender prisms of a brilliant white colour. This salt, according to the analysis of Mr. Porrett, is composed of Hydro-sulpho-evanic acid

30.1

	•	•	
Barytes	•	•	69.9
			100.0
Doubtless the true constituents a	are		
l atom sulpho-cyanogen	•	•	7.25
latom barium	•	•	8.5
			15.75

- 5. Sulpho-cyanodide of strontium. A deliquescent salt, crystallizing in long slender prisms in groups, radiating like zeolite.
- 6. Sulpho-cyanodide of calcium. A deliquescent salt, soluble in alcohol, from which it may be obtained in a mass of needle-form crystals.
- 7. Sulpho-cyanodide of magnesium. A deliquescent, incrystallizable salt. When dried it has a micaceous appearance.
- 8. Sulpho-cyanodide of aluminum. It crystallizes in octahedrons, and does not deliquesce.
- 9. Hydro-sulpho-cyanate of iron. This salt may be obtained by dissolving iron in an aqueous solution of hydro-sulphocyanic acid. It has a light bluish green colour, a sweet and astringent taste, and reddens litmus paper. The salt is very soluble in water. The solution becomes red when exposed to

Class VI. the air, or when mixed with chlorine, nitrous acid, &c. and at the same time deposites a yellow ochre, consisting of a subsalt.

- 10. Hydro-sulpho-cyanated peroxide of iron. A salt of a beautiful crimson colour, deliquescent, and only obtainable in a solid form by exposure to an atmosphere artificially dried. When in a solid state it appears black by reflected light.
- 11. Sulpho-cyanodide of mattyanese. A colourless salt, very soluble in water,\* but almost insoluble in absolute alcohol.
- 12. Sulpho-cyanodide of nickel. Very soluble in water.+
- 13. Sulpho-cyanodide of covalt. It may be obtained by mixing an aqueous solution of sulphate of cobalt with the alcoholic solution from which sulpho-cyanodide of potassium has been precipitated. The sulpho-cyanodide shoots into blue coloured prisms, which, when exposed to the air, become first violet and finally of a rose red colour. By the addition of water, they become nearly colourless; but alcohol restores the blue colour again.t
  - 14. Sulpho-cyanodide of zinc. Very soluble in water.§
- 15. Sulpho-cyanodide of lead. It crystallizes in rhombohedrons, and deliquesces in a moist atmosphere.
  - 16. Sulpho-cyanodide of tin. Very soluble in water.
- 17. Hydro-sulpho-cyanate of suboxide of copper. may be obtained by digesting hydrated suboxide of copper in hydro-sulpho-cyanic acid. It is a white powder, insoluble in water and in most acids, decomposable by alkalies, or by distillation with sal ammoniac; also by mixture with pernitrate of iron. When mixed with five times its weight of chlorate of potash it explodes by heat, friction, the contact of sulphuric acid, or the electric spark. This salt, according to the analysis of Mr. Porrett, confirmed and amended by the subsequent analysis of Berzelius, is composed of

1 atom hydro-sulpho-cyanic acid 1 atom suboxide of copper

16 375

18. Sulpho-cyanodide of copper. This salt may be formed by mixing together solutions of sulpho-cyanodide of soda and sulphate of copper. It is then in the state of a bright peagreen liquid, to which, if any deoxidizing substance, as sulphurous acid, an alkaline sulphite, or the salts of protoxide of

<sup>\*</sup> Porrett. + Idem. 1 Grotthuss. § Porrett. | Idem. ¶ Idem.

Sect. V.

tin or iron be added, the hydro-sulpho-cyanated suboxide falls in the state of a white powder.\*

19. Sulpho-cyanodide of bismuth. Very soluble in water.

20. Disulpho-cyanodide of mercury. When solutions of sulpho-cyanodide of potash and nitrated suboxide of mercury are mixed a white precipitate falls. When this matter is dried in a temperature below ignition, it suddenly swells up (while azotic gas, bisulphuret of carbon, and mercurial vapours are given off,) to a mass, consisting of frothy plates, resembling graphite, still containing cyanogen, and which is neither attacked by boiling potash nor by most of the acids; but which nitric acid first renders yellow and then dissolves, while deut-oxide of azote is disengaged, and which, by an additional heat, is converted into cinnabar.

When red oxide of mercury is dissolved in hydro-sulphocyanic acid and the solution concentrated, white irregular prisms are deposited, having a sharp metallic taste. The residue being heated, gives out, with much violence, azotic gas, bisulphuret of carbon, and a peculiar gas, (probably sulpho-cyanogen); finally, cinnabar sublimes, and there remains a yellowish or brownish substance.‡

- 21. Sulpho-cyanodide of silver. When solutions of sulpho-cyanodide of potassium and nitrate of silver are mixed, a white curdy precipitate falls, which is the salt in question. When exposed to the light it blackens; but not so much as chloride of silver. An aqueous solution of chlorine decomposes it into chloride of silver, sulphur, ammonia, and carbonic acid. § It is soluble in ammonia.
- 22. Sulpho-cyanodide of gold. Sulpho-cyanodide of potassium, when mixed with a solution of chloride of gold, throws down a flesh-red precipitate, which, according to Grotthuss, when treated with muriatic acid, becomes purple. The alkalies expel some hydro-sulpho-cyanic acid, and give it a yellow colour. It dissolves in a solution of sulpho-cyanodide of potassium with a purple colour. It dissolves readily in liquid ammonia.
- 23. Sulpho-cyanodide of platinum. A yellowish white bulky precipitate, readily soluble in acids, and in aqueous solutions of the alkaline muriates, from which it is again thrown down by alcohol in yellowish white flocks.
  - 24. Sulpho-cyanodide of palladium. Very soluble.¶
    - \* Porrett. † Wöhler, Gilbert's Annalen, lxix. 272.
    - ‡ Berzelius. 

      Grotthuss. 

      Id. 

      Porrett.

- 25. Sulpho-cyanodide of chromium. Very soluble.\*
- 26. Sulpho-cyanodide of uranium. Very soluble in water,+ insoluble in alcohol.
  - 27. Sulpho-cyanodide of molybdenum. Very soluble.§

#### SECTION VI. OF BISULPHO-CYANODIDES.

This genus of salts is still almost unexplored, a few only have been noticed by Wöhler.

- 1. Bisulpho-cyanodide of potassium. An excess of aqueous solution of potash is poured upon hydro-bisulpho-cyanic acid, the salt precipitates. Pour off the yellow liquid, and wash the salt with alcohol. A red, translucent, brittle matter is obtained, which is the salt in question. When heated, sulphur is disengaged, and sulpho-cyanodide of potassium remains. It dissolves readily in water, and slightly in liquid potash.
- 2. Bisulpho-cyanodide of barium. Hydro-bisulpho-cyanic acid is but little soluble in barytes water.
- 3. Bisulpho-cyanodide of lead. The salts of lead give with a solution of bisulpho-cyanodide of potassium, a lemon yellow precipitate.
- 4. The nitrated suboxide of mercury produces a similar precipitate.
- 5. Nitrate of silver when mixed with the same saline solution, gives a dark yellow precipitate.

## SECTION VII. -- OF PRUSSIATES, OR FERRO-CYANODIDES.

I have given an account of the hydro-ferro-cyanic acid in page It is well known that the salt formerly 249 of this volume. known by the name of phlogisticated alkali, afterwards by that of prussiate of potash, and which Mr. Porrett more lately designated by the name of ferro-chyazic acid, has the property of precipitating the greater number of the metals from their acid solutions, and these precipitates are distinguished by a variety of colours characterizing the particular metals. Whether this hydro-ferro-cyanic acid be a peculiar compound acid, or whether it be merely a solution of an atom of cyanodide of iron, in two atoms of hydro-cyanic acid, has not been yet determined. But there can be no doubt that a set of double cyanodides exist, one of the constituents of which is always cyanodide of iron. I shall give an account of these double salts in the present section.

Sect. VII.

1. Hydro-ferro-cyanate of ammonia. This salt was discovered by Macquer. It forms hexangular crystals of a light lemon-yellow colour, is very soluble in water, and deliquesces when exposed to the air. It has not been analyzed, but is probably a compound of

2 atoms hydro-cyanate of ammonia	•	•	11
1 atom cyanodide of iron	•	•	6.75
		•	
,			17.75.

2. Ferro-cyanodide of potassium. This salt which is the most important of all the double cyanodides, has been described in page 249 of this volume. Its constituents are

2 atoms cyanodide of potassium	•	•	16.5
1 atom cyanodide of iron	•		6.75
3 atoms water	•	•	3.375
			<del></del>
			26.625

3. Red ferro-cyanodide of potassium. This salt was discovered by M. L. Gmelin, and described by him in the year 1822.\* Mr. Johnston obtained it in minute quantities in 1827, and in 1828 laid an account of its properties and an analysis of it before the Royal Society of Edinburgh, which was afterwards published in the Edinburgh Transactions.† The easiest method of procuring this salt, is to reduce the preceding salt to powder, and to expose it to an atmosphere of dry chlorine gas till its colour becomes dark red. It is then to be dissolved in water and crystallized. The crystals obtained consist of the new salt.

The crystals have an aurora red colour, are transparent, and consist of doubly oblique prisms, the faces of which are inclined to each other at angles of about 100° and 80°. The prism is usually terminated by a four-sided pyramid, the faces of which are inclined to the corresponding faces of the prism, at angles of 137°. The powder of this salt is orange yellow. It has a weak, astringent, and saline taste. It does not act upon vegetable blues. The crystals decrepitate when heated, and fall down in the state of a brown powder, give out cyanogen gas with some azotic gas, and leave a grayish black porous matter, from which water extracts cyanodide of potassium, prussiate of potash, and tercarburet of azote. When sulphuric acid is poured on this salt it gives out chlorine, and when heated,

hydro-cyanic acid gas. M. L. Gmelin concluded from his experiments, that this salt is a compound of

3 atoms potassium	•	•	15
2 atoms iron	•	•	7
6 atoms cyanogen	•	•	19.5
•			41.5

But from the experiments of Mr. Johnston it is evident that these constituents cannot represents the true constitution of the salt. He found that when common prussiate of potash was exposed to the action of chlorine, nothing was given out except water, and that 26.625 grains of the salt lost, when thus treated, 3.375 grains of water, and gained almost exactly 2.25 grains by the absorption of chlorine. Now 2.25 is half an atom of chlorine. It appears from this, if we can confide in Mr. Johnston's experiments, that the only difference between this salt and the common prussiate of potash is the substitution of half an atom of chlorine for the three atoms of water which that salt contains. Hence its constituents are

2 atoms cyanodide of potassium	•		16.5
1 atom cyanodide of iron	•		6.75
$\frac{1}{2}$ atom chlorine	•	<b>~</b> .	2.25
		•	
			25.5

In what way the chlorine exists in the salt, has not yet been explained in a satisfactory manner.

4. Ferro-cyanodide of sodium. This salt may be formed by a process similar to that for forming ferro-cyanodide of potassium, substituting soda for potash. For the first detailed description of it we were indebted to Dr. John. Its colour is yellow. It crystallizes in four-sided prisms terminated at both extremities by dihedral summits. They are transparent and have a bitter taste. When left in a warm place they fall down in the state of a white powder, and lose  $37\frac{1}{2}$  per cent. of their weight. At the temperature of  $55^{\circ}$  they require  $4\frac{1}{2}$  times their weight of water to dissolve them, but they are much more soluble in boiling water, a portion of the salt crystallizing as the solution cools. The specific gravity of the crystals is 1.458. They are soluble in alcohol.\* Its constituents, as determined by the analysis of Berzelius, are as follows:

<sup>\*</sup> Gehlen's Jour. 2d series, iii. 171.

2 atoms cyanodide 1 atom cyanodide		•	•	12·5 6·75	Sect. VII.
•	•	•	•	13.5	
ı				32.75	

5. Ferro-cyanodide of barium. For the first accurate description of this salt we are incepted to Dr. Henry. It may be formed by adding prussian blue to hot barytes water till it ceases to be discoloured. The solution, when filtered and gently evaporated, yields crystals of ferro-cyanodide of barium.

These crystals have the figure of rhomboidal prisms, they have a yellow colour, and are soluble in 1920 parts of cold water, and in about 100 parts of boiling water. In a red heat they are decomposed, the acid being destroyed. They are soluble in nitric and muriatic acids, sulphuric acid occasions a precipitate of sulphate of barytes.\* According to the analysis of Porrett, rectified by the subsequent experiments of Berzelius, its constituents are

2 atoms cyanodide	e of b	arium	•	•	23.5
1 atom cyanodide	of ire	on	•	•	6.75
6 atoms water	•	•	•		6.75
					·
					37.00

- 6. Ferro-cyanodide of strontium. This salt was also first examined by Dr. Henry. It may be formed by the same process as the last species, but the solution does not crystallize nearly so readily. When evaporated to dryness it does not deliquesce, and is again soluble in less than four parts of cold water.+
- 7. Ferro-cyanodide of calcium. This salt was perhaps first mentioned by Mr. Hagen, thut we are indebted to Morveau for the first accurate account of its properties and preparation.

Upon two parts of prussian blue of commerce, previously well washed with a sufficient quantity of boiling water, to separate all the foreign salts, about 56 parts of lime water are to be poured, and the mixture must be boiled for a short time till the lime is saturated with the ferro-cyanic acid, which is known by its no longer altering paper stained with turmeric, it is then to be filtered.

This liquid, which contains the ferro-cyanodide of calcium in solution, has a greenish yellow colour, its specific gravity is

<sup>\*</sup> Nicholson's Jour. iii. 170.

<sup>+</sup> Ibid. 171.

<sup>‡</sup> Crell's Annals, 1784, i. 291.

<sup>§</sup> Encyc. Method. Chim. i. 242.

orated to dryness it yields small four-sided prisms with truncated angles, soluble without alteration in water. It is insoluble in alcohol. Its constituents, according to the analysis of Berzelius, are

31.75

- 8. Ferro-cyanodide of magnesium. When equal weights of prussian blue and magnesia are long digested in a flask containing a sufficient quantity of water, we obtain a yellow solution, which, when evaporated deposites small tabular crystals of ferro-cyanodide of magnesium. They deliquesce in the air.\*
- 9. Ferro-cyanodide of aluminum. This salt is obtained by digesting hydrated alumina in a solution of hydro-ferro-cyanic acid. The compound formed, if neutral, is but little soluble in water, but it dissolves readily if it contain an excess of acid.
- 10. Ferro-cyanodide of glucinum. It may be obtained by mixing together ferro-cyanodide of lead and sulphate of glucina, and after decomposition has taken place, filtering the liquid and evaporating. A transparent variable is obtained, easily soluble in water, and often tinged blue from a commencement of decomposition.
- 11. Ferro-cyanodide of yttrium. It is obtained by mixing together solutions of common prussiate of potash and muriate of yttria. A white precipitate falls, which after a certain time becomes pearl gray. It is insoluble in water and acetic acid, but according to Klaproth, it dissolves in muriatic acid.
- 12. Ferro-cyanodide of cerium. Obtained by a similar process as the last salt. A white precipitate soluble in nitric acid.
- 13. Prussian blue. This beautiful pigment is formed by mixing solutions of common prussiate of potash and green sulphate of iron together. A light blue precipitate falls, which is washed several times a day with cold water for several weeks. The colour gradually deepens, till it becomes at last of an intense blue, with a kind of metallic lustre. If the sulphated peroxide of iron be taken, the precipitate while moist is a fine blue, but on drying it becomes black, and is destitute

of beauty. The solution of protoxide of iron gives a white Sect. VII. precipitate, which becomes gradually blue by exposure to the air. It is tasteless and destitute of combined water, but it holds water lodged in its pores with so much obstinacy, that it cannot be freed from it unless it be exposed to a temperature of 275° at least. When heated cautiously its colour becomes lighter, and at last almost white and it gives out carbonic oxide gas, carbonic acid gas, hydro-cyanic acid, and ammonia. When heated to about 400° in the open air it catches fire and burns like tinder, while carbonate of ammonia is disengaged. nitric and sulphuric acids destroy it. Cold muriatic acid does not act upon it, but this acid when hot deprives it at first of its blue colour, which it recovers again, while some hydro-cyanic acid is disengaged, and some iron dissolved by the acid. aqueous solution of sulphuretted hydrogen in close vessels renders prussian blue white. In cold sulphuric acid it becomes white and gelatinous without dissolving. Prussian blue is insoluble in water, alcohol, ether, oils, and dilute acids. constituents, according to the analysis of Berzelius, (which is most accurate) are

> atom iron 3.5atom cyanogen 3.25 $l_{o}^{1}$  atom water 1.7875

From the phenomena of its formation mentioned above, I think it probable that it is a hydro-cyanate, and a compound of 1 atom hydro-cyanate of iron, and 2 atoms of hydro-cyanated On that supposition (which accords better peroxide of iron. with the analysis than the preceding statement), prussian blue will be a compound of

1	atom	hydro-cya	ınate of	iron	•	•	7.875
2	atoms	hydro-cy	ranated	perox	ide of	iron	16.75
$1_{2}^{1}$	atoms	water	•	•	•	•	1.7875

26.4125

Common prussian blue contains a considerable mixture of alumina, because the pigment is made by the addition of alum to the two substances which are essential to the formation of the prussian blue.

When green muriate of iron is mixed with common prussiate of potash, a white precipitate falls, which gradually becomes blue by exposure to the air (while the liquid remains neutral). The prussian blue thus formed is soluble in water. It must therefore be washed by a solution of sal ammoniac.

The aqueous solution of this prussian blue is not precipitated by boiling or by alcohol; but muriatic acid throws it down, and various saline solutions. Sulphuretted hydrogen throws down a black matter, while hydro-ferro-cyanic acid remains in solution. From the analysis of Berzelius, its component parts appear to be precisely the same as those of common prussian blue.

When prussian blue is digested with liquid ammonia, and the filtered solution is left exposed to the air, yellow shining regular octahedrons are gradually deposited. They have a biting and bitter taste, and a smell intermediate between that of hydro-cyanic acid and ammonia. When pure, they are a compound of

1 atom hydro-cyanate of iron . 7.875 2 atoms hydro-cyanate of ammonia 11

18.875

At the same time, with these yellow crystals there are deposited, when the liquid acquires the consistency of a syrup, green needles, which dissolve in water, and may be precipitated by alcohol in the state of a green syrup. Ammonia renders it yellow, but the green colour again appears when the ammonia is driven off, and at the same time a green coloured pigment falls, which has been distinguished by the name of prussian green. Sulphuric and muriatic acid render it blue; but the deoxidizing acids do not possess that property. This prussian green consists of 1 atom protoxide, and 2 atoms peroxide of iron, combined each with hydro-cyanic acid, which has undergone a modification not yet explained.

When the common prussian blue of commerce is digested in water, and the aqueous solution is sufficiently concentrated, it occasionally becomes green. When we saturate the liquid with acetic acid, evaporate and mix the residue with alcohol, there is obtained a dark green uncrystallizable matter, becoming dark gray on exposure to the air. It dissolves in water with a green colour, leaving behind a green powder. This salt is intimately connected with the yellow prussiate of potash. It contains the same proportions of iron and potassium, the difference is owing to the state of the cyanogen, which is undoubtedly the same as in prussian green.

14. Ferro-cyanodide of manganese. Prussiate of potash throws down the salts of manganese white. The precipitate is

neither soluble in water nor acids, in alkalies giving off hydro- eyanic acid and protoxide of iron.

- 15. Ferro-cyanodide of nickel. When a solution of common prussiate of potash is dropt into any of the nickel salts a precipitate falls in the state of milk white flocks, which becomes gradually greenish or dirty red.
- 16. Ferro-cyanodide of cobalt? Prussiate of potash throws down a greenish yellow 'precipitate when dropt into a salt of cobalt, which, on exposure to the air, becomes gradually reddish gray. When heated to about 680° it gives out water and some hydro-cyanate and carbonate of ammonia, while a ferro-cyanodide of cobalt remains. It dissolves in strong sulphuric acid with a red colour. The solution becomes gradually colourless, while a red coloured crystalline powder falls, which, according to Berzelius, is a sulphated ferro-cyanodide of cobalt.
- 17. Ferro-cyanodide of zinc. Prussiate of potash throws down a white powder from the salts of zinc, which is insoluble in water and in acids.
- 18. Ferro-cyanodide of lead. Prussiate of potash throws down a white precipitate from nitrate of lead. When heated it gives out a little water, and ferro-cyanodide of lead remains. In a stronger heat it gives out carbonic acid and hydro-cyanate of ammonia. Sulphuretted hydrogen gas converts it into sulphuret of lead, sulphuret of iron, and hydro-cyanic acid. Its constituents, as determined by the analysis of Berzelius, are

1 atom cyanodide	of ire	on	. •	•	6·7 <b>5</b>
2 atoms cyanodide	of le	ead		•	32.5
3 atoms water	•	•	•		3.375

42.625

19. Ferro-cyanodide of tin. When prussiate of potash is dropt into a salt of the protoxide of tin a white precipitate falls, which, on exposure to the air, becomes yellow by the absorption of oxygen. It is insoluble in water and acids.

When prussiate of potash is added to a salt of the peroxide of tin a brownish yellow precipitate is thrown down, which is insoluble in water and in alkalies, and which, when treated with alkalies, gives out hydro-cyanic acid and protoxide of iron.

20. Ferro-cyanodide of copper. Prussiate of potash throws down from the salts of copper a beautiful brownish red powder, which, when heated, gives out much water, carbonate and hydro-cyanate of ammonia and azotic gas. When digested in ammonia it diminishes in bulk, and becomes green and crys-

talline. Water, by abstracting the ammonia, restores the green colour. Strong sulphuric acid gives the salt a greenish yellow white colour and dissolves a small quantity of it. Water, by removing the acid, again restores the red colour. It is not soluble in other acids nor in water. The alkalies abstract hydro-cyanic acid and protoxide of iron, while hydrated oxide of copper separates.

- 21. Ferro-cyanodide of mercury. Prussiate of potash throws down from corrosive sublimate precipitate, which, in boiling water, gives out cyanodide of mercury, while cyanodide of iron remains undissolved.
- 22. Ferro-cyanodide of silver. Prussiate of potash throws down a white precipitate from nitrate of silver, which becomes bluish when dried, or even when simply exposed to the air. When heated, it gives off first the cyanogen combined with the silver, then the azotic gas of the cyanodide of iron, burns, and is converted into a mixture of silver and bicarburet of iron.\* It dissolves in strong sulphuric acid, with the exception of a yellow matter which remains behind. The colourless solution becomes black when exposed to the light, and deposites crystalline grains of sulphate of silver. The other acids (even muriatic acid) do not decompose it. Potash throws down oxide of silver, and converts it into common prassiate of potash. Hence it is evident that it is composed of

1 atom cyanodide of iron			<b>6·75</b>
2 atoms cyanodide of silv	er .		34
3 atoms water .		•	3.375

44.125

‡ Id.

- 23. Ferro-cyanodide of gold. Auro-cyanodide of potassium precipitates the protosalts of iron green.+
- 24. Ferro-cyanodide of arsenic. When a solution of arsenious acid in muriatic acid is mixed with liquid prussiate of potash, a white precipitate falls, not soluble in water, but decomposed by boiling nitric acid, which changes the arsenious into arsenic acid and destroys the cyanogen.
- 25. Ferro-cyanodide of chromium. Prussiate of potash throws down the salts of chromium in green flocks, the nature of which has not hitherto been examined.
- 26. Ferro-cyanodide of uranium. Prussiate of potash precipitates the neutral solutions of uranium in beautiful brownish red flocks, darker than ferro-cyanodide of copper.

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27. Ferro-cyanodide of molybdenum. Prussiate of potash, when dropt into salts of protoxide of molybdenum, throws down a dark brown precipitate, which is soluble in an excess of prussiate of potash and also in liquid ammonia with a dark brown colour.

A brown powder, similar in appearance, is thrown down by prussiate of potash from the salts of deutoxide of molybdenum, but it is not soluble in an excess of prussiate of potash.

When prussiate of potash is mixed with a solution of molybdic acid in a stronger acid, a reddish brown precipitate falls, paler than the two preceding ones. It dissolves in an excess of prussiate of potash with a dark reddish brown colour. In liquid ammonia it dissolves, and the solution is almost colourless.\*

- 28. Ferro-cyanodide of titanium. Prussiate of potash throws down the salts of titanium of a yellowish brown colour.
- 29. Ferro-cyanodide of columbium. When prussiate of potash is mixed with a solution of muriate of columbium a deep yellow precipitate falls, which, after being washed and dried, becomes dark brown. It is not altered by exposure to the air or by the action of boiling water.

Iron is not the only metal which combines with potassium into a double cyanodide. Probably all the other metals are capable of replacing iron, and of making with potassium a double cyanodide, which, like prussiate of potash, is capable of entering into combination with other cyanodides, and of forming new classes of double cyanodides. The following 8 of these salts have been already formed.

- 1. Manganese-cyanodide of potassium,
- 2. Nickel-cyanodide of potassium,
- 3. Cobalt-cyanodide of potassium,
- 4. Zinc-cyanodide of potassium,
- 5. Copper-cyanodide of potassium,
- 6. Mercury-cyanodide of potassium,
- 7. Silver-cyanodide of potassium,
- 8. Tellurium-cyanodide of potassium.

These salts are some of them colourless, and some of them yellow. They usually crystallize, and the crystal is most commonly an octahedron, or a rhombohedron. Each of these

salts might be used like common prussiate of potash, to throw down the different metallic salts, and the double cyanodides formed, are distinguished by a different set of colours, and different properties, from those that have been described in this section; but they have not been examined sufficiently in detail to enable us to describe them here. But it must be obvious at a glance, how very much shese different genera of double cyanodides will hereafter increase the number of cyanogen salts.

# CLASS VII.

#### OF SULPHUR ACID SALTS.

The investigation of this class of salts was begun by Berthollet in his paper on sulphuretted hydrogen, published in the 25th volume of the Annales de Chimie. Several additional facts were afterwards added by Vauquelin. But for the generalization of the subject, and for our knowledge of all the genera of sulphur acid salts, except the first, we are indebted to Berzelius. He first pointed out the fact, that sulphur acids, and sulphur bases exist, capable of combining, with each other.\* He afterwards published a numerous and elaborate set of experiments on the sulphur salts, in which he details the properties of nine different genera of these salts, and gives a notice of three other genera.+ I have already, in page 256 of this volume, mentioned, that I proposed to distinguish those combinations of sulphur and a base, which possess acid properties, by the name of sulphides, and those that possess alkaline properties, by the name of sulphurets. Thus, sulphide of hydrogen (the body hitherto distinguished by the terms, sulphuretted hydrogen, hydro-sulphuric acid, &c.) is an acid compound of sulphur and hydrogen; while sulphuret of copper is an alkaline compound of sulphur and copper. Sulphur acids, and sulphur bases, are capable of uniting without decomposition, and of forming various genera of salts, many of which are soluble in water, and are capable of crystallizing. In naming these salts, it is obvious that we must abbreviate the name both of the acid and base, otherwise the terms would be too cumbersome

Nomenclature.

<sup>\*</sup> Kong. Vet. Acad. Handl. 1821, p. 145.

<sup>†</sup> lbid. 1825, p. 232, and 1826, p. 53.

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for use, and would be altogether unsuitable to the idiom of the English language. But we may apply the methed which has been hitherto employed for naming the oxygen acid salts. To the base of each sulphur acid terminating in ate, I shall prefix • the syllables sulpho, which will be a sufficient indication that the salt is a sulphur salt. Thus, a sulpho-hydrate is a sulphur salt, whose acid is sulphide of hydrogen. The base of a sulphur salt being always a sulphuret, or an alkaline base united to sulphur, the nature of the salt will always be sufficiently understood, if we simply add the name of the alkaline base without noticing the sulphur, which is constantly present. Thus, sulpho-hydrate of zinc will indicate that the salt is a compound of sulphide of hydrogen and sulphuret of zinc. Should it be hereafter discovered, that various sulphurets, having the same alkaline base, are capable of uniting with the same sulphur acid, it will become necessary to distinguish the various sulphurets which enter into the combination, just as it is necessary to distinguish the various oxides which unite with the same oxygen acid; and a mode similar to that used for distinguishing these different oxides in the preceding part of this work, might easily be applied to the sulphur bases. the present state of our knowledge, however, this is unnecessarv.

#### SECTION I .-- OF SULPHO-HYDRATES.

When sulphide of hydrogen is made to pass into a solution of any oxidized body, for example into a solution of potash or soda, the oxide is always decomposed by the union of its oxygen with the hydrogen of the sulphide, while the base of the oxide unites to the sulphur of the sulphide, and forms a sulphuret of potassium, of sodium, &c. With this sulphuret a new dose of sulphide of hydrogen is capable of entering into combination, and of forming a sulphur salt. It is in this way that sulpho-hydrates are usually formed. Several of them have been long known under the names of hydro-sulphurets, hydrosulphates, hydro-thionates, &c. They are occasionally used as reagents, and are very useful in chemical analyses.

1. Sulpho-hydrate of ammonia. This salt may be obtained by passing a current of sulphide of hydrogen gas and another of ammoniacal gas into a bottle surrounded with ice. It crystallizes in needles, and is transparent and colourless. It is very volatile, and, when kept in a bottle, sublimes gradually to the top of the vessel, where it crystallizes in long transparent

Class VII. plates. By this spontaneous volatilization, it is easily freed from any impurities with which it may be mixed. When exposed to the air, it speedily becomes yellow.\* This salt may be obtained also, according to Berzelius, by distilling sulphuret of potassium mixed with an excess of sal ammoniac and water. Sulpho-hydrate of ammonia has not been hitherto subjected to a rigid analysis. 2 There are probably two, if not more salts, distinguished by the proportions of the constituents. Whether the ammonia be combined with sulphur is not so clear. As ammonia contains no oxygen, it cannot decompose sulphide of hydrogen. I believe, in general sulpho-hydrate of ammonia contains two atoms of base united to one of sulphide, though the neutral combination is also possible.

When equal parts of lime, sal ammoniac, and sulphur, are distilled in a retort, a yellow liquid is obtained, usually distinguished by the name of fuming liquor of Boyle, because first prepared by that philosopher. This liquid constantly emits white fumes, and has a strong ammoniacal and fetid odour. Berthollet ascertained that it owed its property of emitting fumes to a quantity of uncombined alkali. It consists chiefly of sulpho-hydrate of ammonia holding an excess of sulphur. This liquid gradually loses the property of fuming, and deposites likewise its excess of sulphur. It is ther a sulpho-hydrate of ammonia nearly pure.

2. Sulpho-hydrate of potassium. This salt may be obtained by passing a current of sulphide of hydrogen over carbonate of potash heated to obscure redness, till all evolution of water and carbonic acid is at an end. It is a foliated substance of a lemon yellow colour, which deliquesces speedily in the air, and dissolves readily in water, and when the solution is mixed with the stronger acids, sulphide of hydrogen is given out abundantly, without the precipitation of any sulphur. By evaporation it yields crystals, which are transparent and colourless, and crystallizes in large prismatic crystals, not unlike sulphate of soda. They are usually four-sided, and terminated by four-sided pyramids. Sometimes both the prisms and terminating pyramids are six-sided. Its taste is alkaline and extremely bitter. When exposed to the air, it soon deliquesces into a liquid of a syrupy consistence, tinging green all bodies with which it happens to be in contact. But this colour is not permanent, unless some metallic body happens to be in contact. The

<sup>\*</sup> Thenard, Ann de Chim, lxxxiii 134.

crystals have no smell; but when they have deliquesced they emit a fetid odour. They dissolve both in water, and alcohol; and during the solution the temperature of the liquid sinks considerably.\*

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The constituents of this salt (abstracting the water of crystallization, which is still undetermined), are

• 1 atom sulphide of hydrogen	•	•	$2 \cdot 125$
1 atom sulphuret of potassium	• • •	•	.7
`,			9.125

3. Sulpho-hydrate of sodium. This salt may be formed by exposing sodium in an atmosphere of sulphide of hydrogen. It first combines with an atom of sulphur, by decomposing the sulphide and the sulphuret thus formed, absorbs an additional dose of sulphide, and is converted into sulpho-hydrate. We may form it also in the same way as was described for forming the last salt. The aqueous solution crystallizes. I have given an account of this salt in the first volume of this work, page 268; though the view there given of its constitution is probably not quite accurate.

Its crystals are regular octahedrons. The taste is very hot, bitter, and sulphurcous. It is not sensibly altered by exposure to the air for 24 hours, but it slowly deliquesces into a brown liquid. Its alkaline properties are as powerful as those of a strong caustic potash ley. When heated it undergoes the watery fusion, then becomes solid, and finally catches fire and burns like tinder for a long time, with a very low yellow coloured flame. Its constituents are doubtless

			15:+
7 atoms water	•	•	7.875
I atom sulphuret of sodium	•	•	5
1 atom sulphide of hydrogen	•	•	$2 \cdot 125$

4. Sulpho-hydrate of lithium. To obtain this salt sulphate of lithia may be mixed with charcoal and ignited in a porcelain crucible. The residual matter is to be thrown into water, filtered and saturated with sulphide of hydrogen. A colourless solution is obtained. When concentrated in a retort filled

<sup>\*</sup> Vauquelin, Ann. de Chim. xlii. 40.

<sup>†</sup> Phil. Trans. 1827, p. 167. I suppose my analysis to have been erroneous by 0.125 or an atom of hydrogen, which being under one per cent. might have been easily committed.

with hydrogen gas, to the consistency of a syrup, a little carbonate of lithia precipitates. The liquid, when brought to the consistency of a syrup, is honey yellow. When dried in vacuo, over calcined potash, it is gradually converted into an irregular saline mass, which absorbs moisture from the atmosphere, and dissolves readily in alcohol. When concentrated in the open air it deposites long yellow crystals of quater-sulphuret of lithium.

This salt may be obtained by the same process as that described for procuring sulpho-kydrate of potassium.\*

5. Sulpho-hydrate of barium. When hydrate of barytes is

supersaturated with sulphide of hydrogen, and the solution concentrated in a retort filled with hydrogen gas, it deposites crystals of hydrated barytes and of quater-sulphuret of barium. The residual liquid, when cooled to 14° deposites crystals of sulpho-hydrate of barium in long flat prisms, which are white and opaque.+

When sulphate of barytes is converted into sulphuret, by mixing it with charcoal and keeping it red hot in a crucible, if boiling water be poured upon the black mass, and filtered while hot, the green coloured solution thus obtained yields by evaporation a great number of crystals. They are to be separated immediately by filtration, and dried between the folds of filtering paper.‡ They are white, and have a silky lustre. They have usually the form of scales, whose shape cannot be easily ascertained. This compound is soluble in water, and the solution has a very slight tinge of green. Its taste is acrid and sulphurous; and when exposed to the air it is readily decomposed.

- 6. Sulpho-hydrate of strontium. This salt may be obtained by saturating an aqueous solution of sulphuret of strontium with sulphide of hydrogen. The solution evaporated in vacuo, shoots into large striated four-sided prisms, which may be exposed for some days to the atmosphere without undergoing any alteration. When heated they melt, give off water and sulphide of hydrogen, and finally sulphuret of strontium remains behind in the form of a white powder.§

  7. Sulpho-hydrate of calcium. This salt may be obtained in solution by dissolving sulphuret of calcium in an aqueous

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 242. + Ibid. p. 243.

<sup>‡</sup> Berthollet, Ann. de Chim. xxv. 241.

<sup>§</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 244.

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solution of sulphide of hydrogen. At a certain degree of saturation the absorption of the sulphide ceases, and to get any farther quantity taken up, constant stirring is necessary. The solution cannot be made to deposite crystals of sulpho-hydrate of calcium. After the concentration has reached a certain point the sulphide is disengaged, and crystals of sulphuret of calcium shoot out.\*

8. Sulpho-hydrate of magnesium. This salt may be obtained in solution by passing a current of sulphide of hydrogen through water in which hydrate of magnesia is suspended. The solution takes place slowly; but a very concentrated liquid may in this way be obtained. Like the preceding salt, it cannot be obtained in a solid form, for when we attempt to crystallize the liquid the salt is constantly decomposed.†

## SECTION II. -- OF BISULPHO-CARBONATES.

For our knowledge of these salts we are chiefly indebted to Berzelius. Several of them were described in his paper on bisulphide of carbon, published along with Dr. Marcet, in the Philosophical Transactions for 1813. The mistakes into which he fell in that paper were rectified in his paper on the sulphurets of potassium, published in 1821, and still more completely in his paper on the sulphur salts, published in 1825. It is difficult to obtain these salts in a state of complete purity. The best way is to mix a strong sulphur basis with water and bisulphide of carbon in a flask quite filled with the mixture, and to leave it in the temperature of 86° well stopped. The bisulphide gradually combines with the sulphuret.

When dry bisulpho-carbonates are heated they undergo decomposition. The fixed alkaline salts fuse into a liquid black mass, which, when cold, is dark brown, and when digested in water leaves carbon undissolved, while the metal in the state of sexsulphuret is dissolved in the water. The bisulpho-carbonates of the earthy metals and the metals in general are decomposed in such a way, that if the salt contains chemically combined water, bisulphide of hydrogen and sulphur are evolved, and a carbonate remains behind. But in general the bisulphide of carbon flies off and leaves the base in the state of a sulphuret.

When the bisulpho-carbonates are mixed in the solid form with an acid, muriatic acid for example, a red oily-looking

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 245. + Ibid. p. 246.

liquid is obtained, discovered and described by Zeise. It is a compound of sulphide of hydrogen and bisulphide of carbon. Speedily the sulphide of hydrogen dissolves in the water, and leaves the bisulphide of carbon behind in an opaque state.

- 1. Bisulpho-carbonate of ammonia. This salt was first formed and described by Zeise. He saturated alcohol with ammoniacal gas and dissolved bisulphide of carbon in the liquid. In about an hour or an hour and a half a yellow crystalline powder was deposited, which, after being washed with alcohol and ether, constitutes the bisulpho-carbonate of ammonia in a state of purity.\*
- 2. Bisulpho-carbonate of potassium. This salt is best prepared by adding an excess of bisulphide of carbon to an alcoholic solution of hepar sulphuris. The dark red liquid which collects at the bottom is to be evaporated in the temperature of 86° to the consistency of a syrup. It then deposites crystals of bisulpho-carbonate, which speedily deliquesce in the air. When heated to about 150° it parts with its water of crystallization and loses its crystalline appearance, acquiring a darker colour inclining to red. When heated in a distilling apparatus it gives out nothing volatile. At a red heat it melts and is decomposed. In alcohol it dissolves with difficulty.†
- 3. Bisulpho-carbonate of sodium. It forms a yellow salt, crystallizing when highly concentrated, and deliquescing in the air. It dissolves readily in alcohol.
- 4. Bisulpho-carbonate of lithium. This salt is still more soluble in water than either of the two preceding salts. When dried it gives a salt that speedily deliquesces in the air. It dissolves readily in alcohol. §
  - 5. Bisulpho-carbonate of barium. Crystallized sulphuret of barium unites very readily with bisulphide of carbon, and forms a lemon yellow uncrystallizable salt, which coats the inside of the glass and is easily dissolved. The solution has a fine yellow colour. When evaporated in vacuo it deposites small light yellow translucent crystals. If a drop of water be let fall on the salt it becomes in a few minutes red; but this colour disappears on drying.
  - 6. Bisulpho-carbonate of strontium. It is more soluble in water than the preceding salt. The solution has a lighter

<sup>\*</sup> For a detailed account of this salt I refer to Zeise's paper, inserted in Schweigger's Jour. xli. 100.

<sup>†</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 251. ‡ Ibid.

<sup>§</sup> Ibid. p. 252.

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yellow colour, and gives, when evaporated in vacuo, a striated crystalline salt, of a light lemon yellow colour, as if it had effloresced. When moistened it becomes reddish brown, but this colour vanishes on drying, leaving spots of a lighter yellow.\*

- 7. Bisulpho-carbonate of calcium. This salt gives a very deep red solution, which becomes still darker when kept in a close vessel. By evaporating the liquid in vacuo we obtain a yellowish brown saline mass, with evident marks of crystallization. When fully dried by heat it becomes light lemon yellow; but becomes again darker and redder by absorbing moisture. When again dissolved, it leaves a yellow coloured subsalt having a peppery taste. This salt is always formed unless an excess of bisulphide of carbon is employed. The neutral salt dissolves easily in alcohol. It is decomposed by boiling water, depositing carbonate of lime.+
- 8. Bisulpho-carbonate of magnesium. This salt is most easily obtained by adding bisulpho-carbonate of barium to sulphate of magnesia as long as a precipitate continues to fall. The liquid must then be filtered and evaporated in vacuo. The solid salt is lemon yellow, and shows no symptom of crystallization. A portion of it dissolves readily in water, with a deep yellow colour, and a peppery taste. Another portion forms a subsalt, insoluble in cold, but soluble in boiling water, with a light yellow colour. But it is decomposed at the same time, and leaves carbonate of magnesia undissolved.
- 9. Bisulpho-carbonate of iron. This salt may be obtained by mixing solutions of bisulpho-carbonate of calcium and sulphate of iron. It forms a deep wine red liquid, which gradually darkens, and when viewed by reflected light, looks like ink. An excess of the precipitating medium gives the liquid a darker colour. An excess of the protosalt of iron employed, precipitates the compound in the form of a black powder.§
- 10. Bisulpho-carbonate of sesqui-sulphuret of iron. Bisulphocarbonate of calcium, when added to a solution of peroxide of iron, throws down a dark brown precipitate, which speedily collects into a mass. It is insoluble in water, is not altered during drying, and when pulverized, constitutes an amber brown powder. When distilled, bisulphide of carbon passes over at a very moderate heat. When the heat is augmented, sulphur sublimes, and sulphuret of iron remains.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 252. + Ibid. ‡ Ibid. p. 253. § Ibid. p. 254. | Ibid. p. 255.

- 11. Bisulpho-carbonate of manganese. It may be formed in the same way as the two preceding salts. It forms first a dark brown transparent liquid; but gradually the salt is deposited in a light yellow powder, like sulphuret of manganese. This precipitate dissolves with a yellow colour. It does not blacken on the filter like sulphuret of manganese. When distilled, it gives out carbonic acid gas and sulphur, and leaves green sulphuret of manganese soluble in muriatic acid, without any residue of charcoal.\*
- 12. Bisulpho-carbonate of nickel. Formed by the same process as the preceding salts. It forms a deep brownish yellow solution, slightly translucent, and by reflected light, black. The salt falls in 24 hours in the form of a black powder. The supernatant liquid is transparent and yellow.+
- 13. Bisulpho-carbonate of cobalt. Formation the same. Gives a deep olive green solution, which seen by reflected light is black. In 24 hours it deposites a black flocky substance. The neutral liquid is transparent, and of a deep brown colour.
- 14. Bisulpho-carbonate of zinc.§ Forms a very light yellow precipitate, indeed almost white, which when dry is yellow and translucent.
- 15. Bisulpho-carbonate of cadmium. A fine lemon yellow precipitate, which is soluble in water.
- 16. Bisulpho-carbonate of lead. A deep brown precipitate, which, when it is deposited on the glass, appears transparent. The supernatant liquid is deep yellow; but in 24 hours it becomes colourless. The precipitate when dried becomes black, assumes a polish when rubbed, and when distilled gives out bisulphide of carbon, and leaves sulphuret of lead.\*\*
- 17. Bisulpho-carbonate of tin. Forms a fine dark brown precipitate, not altered when dried.++
- 18. Bisulpho-carbonate of bisulphuret of tin. A light yellow precipitate, which becomes deeper coloured when dry. ‡‡
- 19. Bisulpho-carbonate of copper. A deep brown precipitate, almost black, soluble with a dark brown colour in an excess of the precipitating medium. When dry, it becomes

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 254. † Ibid. p. 255.

<sup>‡</sup> Ibid. p. 255.

<sup>§</sup> All the subsequent salts may be obtained by the same process as that described for procuring bisulpho-carbonate of iron.

black; when distilled, it gives out first bisulphide of carbon, Sect. 11. and then sulphur, while sulphuret of tin remains.\*

- 20. Bisulpho-carbonate of bismuth. A dark brown powder, soluble with a beautiful reddish brown colour in an excess of the precipitating medium.+
- 21. Bisulpho-carbonate of mercury. A black precipitate, which is best obtained when an excess of the precipitant is employed. When dried, it is black, and when distilled, gives off cinnabar, without any trace of bisulphide of carbon, which seems to have been driven off during the drying.
- 22. Bisulpho-carbonate of sub-sulphuret of mercury. It falls in the form of a dark brown transparent substance, not unlike the salt of lead. When dried, it becomes black; when distilled, it gives only mercury and cinnabar, without any trace of bisulphide of carbon, which probably was dissipated during the drying.
- 23. Bisulpho-carbonate of silver. A dark brown precipitate, soluble with a deep brown colour in an excess of the precipitant. When dry, it is black, glistening, and difficult to pulverize; when distilled, it gives a little bisulphide of carbon, with a good deal of sulphur, while a sulphuret of silver remains.
- 24. Bisulphoccarbonate of gold. A dark grayish brown precipitate in a muddy liquid, not easily rendered transparent. When dried, it is black; when distilled, it gives off sulphur, and leaves gold blackened with charcoal.
- 25. Bisulpho-carbonate of platinum. A blackish brown precipitate, soluble with a fine yellow colour in an excess of the precipitant. When dry, it is almost black; when distilled, it gives off bisulphide of carbon, and then sulphur, while sulphuret of platinum remains behind.\*\*
- 26. Bisulpho-carbonate of chromium. A grayish green precipitate, so similar to the hydrated oxide, that it cannot be distinguished by its appearance. But when distilled, it gives off bisulphide of carbon, and leaves brown sulphuret of chromium, which in the open air burns with vigour, and is changed into oxide of chromium.++
- 27. Bisulpho-carbonate of uranium. Gives a clear dark brown liquid, which gradually becomes muddy, and deposites

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 256. † Ibid. † Ibid. p. 257. † Ibid. ¶ Ibid. p. 257.

<sup>\*\*</sup> Ibid. †† Ibid. p. 256.

class VI. a light grayish brown precipitate, which seems to be a bisul-pho-carbonate of uranium. The supernatant liquid is yellow.\*

## SECTION III. -- OF SULPHO-ARSENIATES.

These salts consist of combinations of sulphide of arsenic (described in vol. i. p. 313,) with the different sulphurets. This sulphide is a compound of 1 atom arsenic, with  $2\frac{1}{2}$  atoms sulphur. It is therefore analogous in its composition to arsenic acid. For the investigation of these salts, we are indebted to Berzelius. They may be formed in various ways.

Method of forming.

- 1. By digesting a sulphuret with sulphide of arsenic.
- 2. By treating a sulpho-hydrate with sulphide of arsenic.
- 3. When an arseniate is decomposed by sulphide of hydrogen, the oxygen salt is destroyed, and an equal number of atoms of sulphur enter into the salt in place of the oxygen. This decomposition proceeds at first slowly, but becomes at last more rapid, and it is the best method of obtaining in a state of purity, those salts that do not crystallize. The decomposition is completed when the salt is no longer rendered muddy by chloride of barium or calcium. Those arseniates which are soluble in muriatic acid (though insoluble in water), may be decomposed if their basis consists of a metal, which is thrown down by sulphide of hydrogen; for example, arseniate of copper.
- 4. When sulphide of arsenic is dissolved in caustic ammonia, or by means of an earthy hydrate; but in that case, the sulpho-arseniate is mixed with an arseniate, and the sulphide of arsenic is driven off by acids, without any smell of sulphide of hydrogen.
- 5. When sulphide of arsenic is boiled with the carbonates. The carbonic acid may be completely driven off; but in this case, also, there is a mixture of arseniate present.
- 6. When sulphide of arsenic is fused in the dry way with a hydrate or a carbonate, which is present in excess. In that case we obtain a sulpho-arseniate, mixed with a sulphate and an arseniate; while metallic arsenic sublimes.
- 7. When sulphide of arsenic is digested with a solution of quater-sulphuret of potassium. All higher sulphurets produce the same salts, while at the same time sulphur is precipitated.
- 8. When an arseniate is mixed with sulpho-hydrate of ammonia. Ammonia and the excess of sulpho-hydrate are dis-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 255.

tilled off, and the sulpho-arseniate remains in the retort. This Sect. III. method answers only with those salts whose bases are not precipitated by ammonia.

The colour of the sulpho-arseniates having an alkaline metal Properties. for a base, is yellow when anhydrous; the aqueous solutions are nearly colourless. The colour of the metalline salts varies. The taste of these salts is hepatic, and at the same time a very nauseous bitter. When decomposed by an acid they give out a peculiar hepatic odour like the smell of orpiment in linseed Most of theme are insoluble in water. oil varnish. containing the bases of the alkalies and alkaline earths, and a few others, constitute exceptions. They have a strong tendency to form subsalts consisting of an atom of the acid united to  $1\frac{1}{2}$  atom of the base. These subsalts have a strong tendency to crystallize, which is often wanting in the neutral salts. Hence the difficulty of obtaining the neutral salts.

When alcohol is mixed with a concentrated solution of these salts it occasions a peculiar alteration in them. A subsalt containing two-thirds of the sulphide of arsenic is precipitated, commonly in a crystalline state, and the liquid becomes yel-It now holds in solution a bisulpho-arseniate, sometimes mixed with a small portion of the subsalt held in solution. From this spirituous liquor the bisulpho-arseniate may be obtained by hasty evaporation on a flat glass. It leaves a solid matter of a lemon yellow colour, which is decomposed by water, leaving sulphide of arsenic. If the spiritous solution in considerable quantity be concentrated on the sand bath, it gives by slow cooling a light yellow striated or scaly mass, and upon the bottom of the retort is deposited a fine red or reddish yellow powder. The yellow crystallized mass is persulphuret of arsenic, described in p. 314 of the first volume of this work. The red substance deposited in the retort is sulphide of arsenic.

The sulpho-arseniates are decomposed by acids with the evolution of sulphide of hydrogen. If the solution be dilute no effervescence takes place, the liquid merely smells of sulphide of hydrogen. Even carbonic acid gas passed through the solutions of these salts throws down sulphide of arsenic.

The sulpho-arseniates have a great tendency to form double salts with each other, and this disposition is most remarkable in those which have a tendency to unite when in the state of oxygen salts. Thus sulpho-arseniates of sodium and ammonia unite into a crystallized double salt.

When these salts are heated to redness in an open vessel they are easily decomposed, sulphurous acid and arsenious acid are given out, and a sulphate remains without any trace of an arseniate.

1. Sulpho-arseniate of ammonia. The neutral salt left to spontaneous evaporation dries to a viscid and glutinous mass, which is yellow with a shade of red. It does not harden, and cannot be completely dried without decomposition. When heated in a retort it first melts, gives out some water, and then a yellow liquid distils over, which contains bisulphuret of ammonia, and sulphuret of arsenic remains, which is at last sublimed without residue.

The subsalt is obtained most advantageously when the neutral salt is mixed with sulpho-hydrate of ammonia, and this mixture, after being gently heated, is diluted with alcohol and shaken. During the cooling of the solution the salt shoots into prisms which are colourless, and which when washed with alcohol, and dried between folds of blotting paper, remain nearly unaltered in the air, only becoming yellow on the surface. It is composed (abstracting the water of crystallization), according to Berzelius, of

1 atom sulphide of arsenic,

3 atoms sulphuret of ammonia.

The bisulpho-arseniate of ammonia is obtained in solution in alcohol when the neutral salt is thrown down by that liquid.

Sulphide of arsenic is dissolved by concentrated ammonia, but decomposed by dilute ammonia. Even concentrated ammonia leaves some sulphur undissolved. When sulphide of arsenic is left in ammoniacal gas the gas is absorbed, and the mass converted into a salt, which is sulpho-arseniate of ammonia. Its colour is feebly yellowish. It is soluble in water, and the solution in about an hour deposites an abundant yellow precipitate.\*

2. Sulpho-arseniate of potassium. The neutral salt is best obtained by decomposing arseniate of potash by sulphide of hydrogen. Evaporated in vacuo it leaves a viscid yellowish mass which shows some marks of crystallization. In the open air it continues for sometime liquid, but at last congeals into a crystallized mass, from which rhomboidal tables may be extricated.

The subsalt is obtained when the neutral solution is mixed

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 271.

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with alcohol. It becomes milky, and deposites afterwards an oily like liquid, which is a concentrated solution of the salt in question. It is deliquescent. When dried in a gentle heat it becomes a radiated crystallized mass, which again absorbs water from the air.

The bisulpho-arseniate of potassium exists in the alcoholic solution. It cannot be obtained in a solid form as it undergoes decomposition during the evaporation.

When the neutral salt is precipitated by carbonic acid, or when the biarseniate of potash is decomposed by sulphide of hydrogen a supersulpho-arseniate of potassium is obtained in the state of a yellow powder. It is a compound of

24 atoms sulphide of arsenic, 1 atom sulphuret of potassium.

atom surphite or potassium	
The neutral salt is a compound of	
l atom sulphide of arsenic	9.75
1 atom sulphuret of potassium .	7
	16.75
The subsalt of	
1 atom sulphide of arsenic	9.75
$1\frac{1}{2}$ atom sulphuret of potassium .	10.5
	20.25
The bisalt of	
2 atoms sulphide of arsenic	19.5
l atom sulphuret of potassium .	7
	26.5
While the supersalt consists of	
24 atoms sulphide of arsenic	234
1 atom sulphuret of potassium .	7
	241*

3. Sulpho-arseniate of sodium. The neutral salt may be evaporated to a viscid mass, which, when dried in a moderate heat becomes lemon yellow. It deliquesces in moist air. In a moderate heat it melts in its water of crystallization. This water flies off if the heat be continued, and the salt becomes again solid. The fused mass has little colour, but the cold salt is yellow.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 266.

The subsalt is obtained both when the neutral salt is thrown down by alcohol and when it is mixed with sulpho-hydrate of sodium and left to spontaneous evaporation. Alcohol throws it down in snow white crystalline scales, which may be washed on the filter with alcohol and dried. From its aqueous solution the salt shoots into regular crystals. These are sometimes irregular rhomboidal prisms, sometimes long six-sided prisms somewhat flat with two sharper angles. When very slowly evaporated the crystals are translucent four-sided prisms If the crystallization be effected below with rhombic bases. the freezing point the crystals are translucent octahedrons with rhomboidal bases. This salt is not altered by exposure to the The translucent crystals of it are yellowish, the opaque crystals are milk white. It is very soluble in water. the translucent crystals are slightly heated they lose their water of crystallization and become milk white. strongly heated they become yellow, and some sulphide of hydrogen is disengaged. When heated in a retort it melts in its water of crystallization, forming a light yellow liquid. water then makes its escape, leaving a white salt, which at last undergoes a kind of decrepitation, during which a little sulphide of hydrogen is evolved and the salt becomes yellow. It then melts without decomposition into a dark red liquid, which becomes yellow on cooling, and it is still soluble in From the analysis of Berzelius, it would appear that this subsalt is a compound of

1	atom	sulphide	of a	rsenic	•	•	9.78
$1\frac{1}{2}$	atom	sulphure	t of	sodium	•		7.50
$7\frac{7}{2}$	atoms	water	•	•	•	•	8.4375
							25.6875

Bisulpho-arseniate of sodium is obtained by means of alcohol. It is known only in solution in alcohol, which, when distilled off to a certain quantity often deposites a persulphuret of arsenic in very fine crystallized scales.

A supersulpho-arseniate of sodium is obtained in the same way as the salt of potassium. It is yellow and pulverulent, and has not been analyzed.\*

4. Sulpho-arseniate of lithium. The neutral salt does not crystallize. It may be dried to a lemon yellow mass, which

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 267.

does not absorb moisture in the air, and which dissolves again completely in water.

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The subsalt is precipitated by alcohol in large colourless brilliant crystalline scales, easily soluble in water. When a boiling solution is rapidly cooled they assume the form of six-sided prisms, and by spontaneous evaporation shoot into flat four-sided prisms with rhombic bases. When heated they behave precisely like the sodium salt.

Bisulpho-arseniate of lithium, and supersulpho-arseniate of lithium, resemble very closely the same salts of sodium.\*

5. Sulpho-arseniate of barium. The neutral salt is very soluble in water, and dries to a porous lemon yellow mass, which is still completely soluble in water. If all the water be driven off, it is again absorbed on exposure to the air. This causes it to swell, and to fall down in powder.

The subsalt is quite similar to the neutral. It is obtained when the neutral salt is heated in a retort to redness, by which sulphur and sulphide of arsenic are sublimed, and a fused mass remains, which when cold is brown, and which readily dissolves in water, leaving a brown substance; and it dries into a lemon yellow, not crystallizable mass.

Sexsulpho-arseniate of barium is obtained in the alcohol solution, which, when evaporated, lets fall a yellow powder. It is insoluble in water, and is decomposed by acids with the evolution of sulphide of arsenic. According to Berzelius's analysis, it is a compound of

6 atoms sulphide of arsenic . 58.5 1 atom sulphuret of barium . 10.5

69+

- 6. Sulpho-arseniate of strontium is easily soluble in water, and has quite the characters of the barium salt. When it is mixed with alcohol, we get either a syrup like precipitate, or a white powder. Both are the subsalt, more or less freed from the neutral. It is easily dissolved in water, and resembles the neutral in its characters.‡
- 7. Sulpho-arseniate of calcium. The neutral salt is quite similar to the barium salt. It dries to a clear slightly coloured syrup, which, when the spontaneous evaporation is continued longer, becomes yellow on the edges, and at last hardens to a

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 270.

<sup>†</sup> Ibid. p. 272. • ‡ Ibid. p. 273.

Class VII. yellow translucent mass, which at 160° loses its water, but recovers it again when exposed to the air, during which it swells, cracks, and separates from the glass. A syrupy solution being exposed for some days to a temperature of 14°, did not shoot into crystals, nor did it freeze.

> The subsalt is easily soluble in water, and does not crystal-It is obtained when the neutral salt is digested with an excess of sulphuret of calcium, and the filtered liquid evapora-Alcohol also throws it down from the neutral solution, either in the state of a syrup or a powder, according to the quantity of water which it retains.\*

> 8. Sulpho-arseniate of magnesium. The neutral salt is soluble in water in all proportions, and dries to a lemon vellow mass, with indications of crystallization. It absorbs no water from the air, but remains unaltered. Its aqueous solution is not precipitated by alcohol.

> The subsalt is obtained when the neutral salt is mixed with a solution of sulpho-hydrate of magnesium, as long as sulphide of hydrogen is evolved, and the liquid then evaporated in vacuo. It shoots into colourless needle-form crystals, which deliquesce in the air. Alcohol dissolves from it a neutral calcium salt, and leaves a salt with a still greater excess of base, which is nearly insoluble in water.+

- 9. Sulpho-arseniate of aluminum is a light yellow precipitate. After drying, the earth is taken up by acids, without any smell of sulphide of hydrogen, so that the dry mass is merely a mechanical mixture.t
- 10. Sulpho-arseniate of glucinum, 11. Sulpho-arseniate of yttrium, 3 The neutral salts of these earths are neither precipitated by the neutral nor subsulpho-arseniates, and the hydrates of these earths, digested with sulphide of arsenic, dissolve a portion of it; so that the solutions become yellowish, and let fall sulphide of arsenic when treated with acids.§
- 12. Sulpho-arseniate of cerium. Both the neutral and subsalt are in the state of a light yellow precipitate, which becomes somewhat more yellow in drying.
- 13. Bisulpho-arseniate of cerium. The sulpho-arseniate made by means of the peroxide of cerium, is slightly soluble in water, so that the precipitate does not appear when the solution is

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 274. † Ibid. p. 275. | Ibid. p. 279. ‡ Ibid. p. 276. § Ibid. p. 275.

The precipitate is white, with a slight shade of Sect. III. very dilute. vellow.

- 14. Sulpho-arseniate of zirconium. While moist, it is lemon yellow, but becomes orange on drying; so that the colour of sulphuret of zirconium appears. It is not in the least altered by acids, which dissolve no zirconia out of it.\*
- 15. Sulpho-arseniate of iron is thrown down of a dark brown colour, which speedily becomes quite black. The precipitate dissolves with a dark brown colour in an excess of the precipitant, and forms a dark brown liquid. When dried, it is decomposed, and gives a dark rust coloured matter. A portion of the iron is thereby oxidized, while another portion combines with an additional dose of sulphur, and is changed into the next following salt.+
- 16. Sulpho-arseniate of bisulphuret of iron is thrown down by the neutral salt in the form of a flocky mass, of a dingy gray colour, with a tint of green. The precipitate is partially dissolved by the precipitating medium. The liquid becomes almost black, and leaves undissolved a black matter.‡
- 17. Sulpho-arseniate of manganese is soluble in water, both when it contains two-thirds of sulphide of arsenic, and when it is neutral. The salts of manganese are not precipitated by the sulpho-arseniates. If carbonate of manganese be boiled with newly precipitated and well washed sulphide of arsenic, the carbonic acid is driven off, and a combination takes place. But the best way of obtaining the salt, is to digest newly precipitated and still wet sulphuret of manganese with sulphide of arsenic and water. The greatest part remains in the state of a yellow powder, which dissolves in a greater quantity of water, if it be placed in contact with it. When sulpho-arseniate of manganese is put into strong caustic ammonia, it is decomposed, and a tile red powder remains, which, according to Berzelius's analysis, is a tris-sulpho-arseniate of manganese, being composed of

1 atom sulphide of arsenic .	•	9.75
3 atoms sulphuret of manganese		16.5
		96.958

18. Sulpho-arseniate of nickel. It gives first a clear yellow brown liquid, which afterwards darkens, and is precipitated. This happens both with the neutral and subsalt.

\* Berzelius, Kong. Vet. Acad. Handl. 1825, p. 276. † Ibid. p. 278. § Ibid. p. 276. | Ibid. p. 279. † Ibid.

- 19. Sulpho-arseniate of cobalt. It is obtained in the state of a dark brown powder, which when collected is black, and continues black when dry. It is soluble in an excess of the precipitant, with a dark brown colour.\*
- 20. Sulpho-arseniate of zinc is thrown down in the form of a light yellow bulky powder, which when dried assumes a fine orange colour. The subsalt when thrown down is much less yellow, but when dried, assumes the same colour as the neutral salt.
- . 21. Sulpho-arseniate of cadmium. A light yellow precipitate.
- 22. Sulpho-arseniate of leath. The neutral salt forms a dark brown, the subsalt a fine red precipitate. When collected they become darker, and when dry are black.
- 23. Sulpho-arseniate of tin. A dark chesnut brown precipitate, which retains its colour on drying. The neutral and subsalt are quite alike.
- 24. Sulpho-arseniate of bisulphuret of tin. A light yellow viscid precipitate, both when neutral and when a subsalt. Not easily separated from the water on the filter. When dry, it has a fine orange colour.
- 25. Sulpho-arseniate of copper. A dark brown precipitate, which when dried becomes black. This salt is often formed during analyses, when an acid liquor, containing both arsenic and copper is precipitated by sulphide of hydrogen. If arsenic acid in excess be present, the first precipitate is brown, and consists of sulpho-arseniate of copper; then sulphide of arsenic falls of a yellow colour.
- 26. Sulpho-arseniate of bismuth. Forms a dark brown precipitate, both when neutral and in the state of a subsalt. It is soluble in an excess of the precipitating medium.\*\*
- 27. Sulpho-arseniate of mercury. Whether neutral, or in the state of a subsalt, falls of a dark yellow colour, which is not altered when dried. It may be sublimed without giving off any sulphur. The sublimate is a bright black, and gives a red powder like cinnabar.††
- 28. Sulpho-arseniate of subsulphuret of mercury. If the salt from which it is obtained be free from red oxide of mercury, it gives a black, in the contrary case, a dark yellowish precipitate, which on drying becomes darker. When heated in a retort, it decrepitates violently, and metallic mercury is given out, without any trace of sulphur or cinnabar. The decrepi-

tated salt then sublimes, and is converted into sulpho-arseniate Sect. 111. of mercury.\*

- 29. Sulpho-arseniate of silver falls with a dark brown colour. At first it appears to dissolve in water, but gradually collects together, and appears black. When dried, it constitutes a black mass, whose powder is brown. The neutral and subsalt are quite alike. When distilled, it neither gives out sulphur nor sulphide of arsenic, and in a full red heat, melts into a splendid gray metallic bead, without giving out any volatile This bead is soft, may be indented with the hammer, and cannot be pulverized.
- 30. Sulpho-arseniate of gold is soluble with a reddish brown colour in water. The subsalt is thrown down of a dark brown colour, but is again dissolved when it is washed on the filter. When the solution is mixed with sulphate of iron, a yellowish brown substance falls, and the liquid becomes colourless.‡
- 31. Sulpho-arseniate of platinum forms, whether neutral or in the state of subsalt, a dark yellow solution, which becomes gradually dark brown without any precipitate falling. Sulphate of iron throws down a brown matter, so dark, that it appears black, and the liquid becomes colourless.§
- 32. Sulpho-arseniate of antimony. A bright yellow compound, easily fusible. ||
- 33. Sulpho-arseniate of chromium whether neutral or a subsalt has a muddy yellow, and when dry, an impure fine yellow colour.¶
- 34. Sulpho-arseniate of molybdenum. A fine yellowish brown solution, which becomes darker, but lets fall no precipitate.\*\*
- 35. Ammonia-sulpho-arseniate of sodium. The subsalt is obtained by mixing the two constituents that go to the formation of the double salt, and diluting the liquid with alcohol, and then agitating the whole. During the cooling, small foursided tables shoot upon the inside of the glass. When subsulpho-arseniate of sodium is dissolved in very little water, and sal ammoniac in the requisite quantity is added to the solution, the double salt gradually shoots into six-sided prisms, with two broad faces, having a slightly yellowish colour. The salt is not altered by exposure to the air. When distilled, sulphuret of ammonia and a little water passes over, and sulpho-arseniate of sodium remains. According to the analysis of Berzelius, this double salt is a compound of

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 280. † Ibid. p. 280.

<sup>‡</sup> Ibid. p. 281. § Ibid. || Ibid. ¶ Ibid. \*\* Ibid.

1 atom subsesqui-sulpho-arseniate of sodium,

I atom tris-sulpho-arseniate of ammonia.

It is much more easily dissolved in water than the sodium salt alone.\*

- 36. Ammonia-sulpho-arseniate of magnesium is formed when solutions of the two salts in alcohol are mixed. In a few minutes a subsalt falls in fine white crystalline needles. It is slowly decomposed by exposure to the air, to a neutral salt, and becomes yellow. It dissolves readily in water, and gives out sulphuret of ammonia if the liquid be heated. When left to spontaneous evaporation, it dries to a yellow mass, not crystallized, and soluble in water.+
- 37. Sodium-sulpho-arseniate of potassium. It is made by mixing together the two saline constituents. The subsalts crystallize together in very regular, colourless, or slightly yellowish crystals, in shape quite similar to that of the two preceding double salts.

## SECTION IV .-- OF SULPHO-ARSENITES.

These salts consist of compounds of orpiment, which might be called sesqui-sulphide of arsenic, and the alkaline sulphurets. They may be obtained in the same way as the sulphoarseniates, substituting for arsenic acid and sulphide of arsenic, arsenious acid and orpiment. They are formed exclusively by the dry way, and cannot be obtained by means of the alkaline sulphurets.

Alkaline sulpho-hydrates dissolve orpiment only till the solution contain a bisulpho-arsenite. The sulphurets of barium, calcium, and magnesium, take up a very inconsiderable excess of orpiment.

These salts (when the bases are colourless), whether neutral or in the state of subsalts, are colourless, and have only a slight tint of yellow. The salts with coloured bases, have, in general, the same colours as the sulpho-arseniates, their taste and smell are also similar.

They are best obtained either in a solid form, or in a dilute solution. The subsalts may be kept better than the neutral or supersalts. When a solution of these salts is evaporated, it begins at a certain degree of concentration, to assume a brownish yellow colour. It then deposites a brown powder, which in-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 282. † Ibid. ‡ Ibid.

<sup>§</sup> This sulphide is analogous in its composition to arsenious acid. Hence the reason for distinguishing this genus of salts by the name sulpho-arsenites.

Sort TV

creases till the salt dries, when it is in a great measure decomposed into sulpho-arseniate and subsulpho-arsenite. Water dissolves only the first of these salts leaving the second, which, however, may be taken up by boiling water. Alcohol produces a similar decomposition.

Orpiment dissolves easily in caustic potash or soda. The cold solution is nearly colourless; when boiled it assumes a dark brown colour, and at last deposites a dark brown powder, which, when dry, is almost black.

The sulpho-arsenites with an alkaline basis, are not decomposed at a red heat in a retort. The others lose more or less of their orpiment. By alcohol they are decomposed in the same way as the sulpho-arseniates. The subsalts which are thrown down by alcohol, are obtained only when the solution is not fully saturated with orpiment. By acids they are altered in a way analogous to the sulpho-arseniates. Easily reducible oxygen bases or oxides form with them in the cold arsenites, and when boiled with them arseniates, while the reduced metal unites with the sulphur, producing a sulpho-arseniate.

The solutions, when exposed to the air, undergo similar alterations with the sulpho-arseniates, but they deposite no sulphur.

1. Sulpho-arsenite of ammonia is obtained when orpiment is dissolved in sulpho-hydrate of ammonia, or in caustic ammonia. It is decomposed by spontaneous evaporation, and leaves a brown powder, consisting of a mixture of orpiment, with a lower degree of sulphide of arsenic. Orpiment is dissolved when boiled with carbonate of ammonia.

When a solution of the neutral salt in water is mixed with alcohol, a white crystalline precipitate falls, which speedily becomes brown. But if the liquid be first mixed in an excess of sulpho-hydrate of ammonia, we obtain a milky liquid which afterwards becomes clear, while light feather-shaped crystals are deposited, constituting a subsalt composed of

l atom sesqui-sulphide of arsenic	••	•	7.75
3 atoms sulphuret of ammonia	•	•	15.375
			93.195

When collected on a filter, and washed with alcohol, they are white, but become yellow in the air while sulphuret of ammonia is evolved, and at last orpiment only remains.\*

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 286.

2. Sulpho-arsenite of potassium,3. Sulpho-arsenite of sodium,

are obtained only in dilute

4. Sulpho-arsenite of lithium, 3 solutions, or in an anhydrous form, by preparing them in the dry way.

If orpiment be fused with carbonate of potash, and the excess of orpiment be driven off, we obtain bisulpho-arsenite of potassium, from which water takes up a neutral sulpho-arsenite, and leaves a red undissolved matter consisting of sulphuret of potassium saturated with orpiment, and a hyposulpho-arsenite of potassium. Caustic ammonia dissolves the first of these salts and leaves the second.\*

- 5. Sulpho-arsenite of barium forms an almost colourless liquid, which dries to a gummy like substance, and assumes a fine reddish brown colour. It dissolves again completely in water without communicating colour. Alcohol throws down from the solution a subsalt in crystalline plates. It is formed also when orpiment is digested with an excess of sulphuret of barium. It dissolves with difficulty in water, and when evaporated in the open air deposites fine white flocks of a subsalt mixed with minute crystals of sulphate of barytes.†
- 6. Sulpho-arsenite of calcium is formed by macerating orpiment with hydrate of lime and water, the arsenite of lime which is formed at the same time, remaining undissolved. The solution is colourless, and when left to spontaneous evaporation deposites fine feather-shaped crystals of a subsalt, mixed with which occurs the neutral salt in the state of a brown matter, not crystallized. If the neutral salt be mixed with more orpiment, it takes up an additional portion and becomes yellow, but soon begins to deposite a brown powder. If it be now left to spontaneous evaporation, it becomes light brownish red, andleaves, when dissolved, subsulpho-arsenite of calcium behind.

If alcohol be mixed with a filtered solution of a salt with excess of sulphuret of calcium we obtain a white crystalline precipitate composed, according to the analysis of Berzelius, of

						100.00
45						
Water	•	•	•	•	•	36.65
Sulphuret of calcium			•	•	•	29.80
Orpiment	•	•	•	•	•	33.55

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 285.

This is obviously equivalent to

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22.9375

• 7. Sulpho-arsenite of magnesium is easily soluble in water. When the solution is evaporated it becomes light brown, assumes the form of a clammy mass, which at last dries, and is no farther altered in the air. • Every time it is dissolved and evaporated it leaves a little brown hyposulpho-arsenite.

It dissolves completely and easily in alcohol. If a concentrated aqueous solution be left in the temperature of 23° it deposites colourless needles of hyposulpho-arsenite, and a dark reddish brown mass of sulpho-arsenite of magnesium.\*

- 8. Sulpho-arsenite of glucinum gives a light yellow precipitate without the smell of sulphide of hydrogen. The supernatant liquid is yellow, a proof that the precipitate is soluble in it. The precipitate retains its colour when dried. Caustic ammonia dissolves the orpiment and leaves the regenerated earth.†
  - 9. Sulpho-arsenite of aluminum } exhibit the same pro10. Sulpho-arsenite of yttrium } perties.‡
- 11. Sulpho-arsenite of cerium gives a very fine orange precipitate like chromate of lead. The supernatant liquid is yellow. The colour becomes still finer when the precipitate is dried. It fuses in an incipient red heat and becomes translucent. After this it gives out a portion of orpiment, but continues in fusion and retains its transparency. The fused mass when roasted in the open air is easily changed into a sulphate.
- 12. Sulpho-arsenite of zirconium forms an orange yellow precipitate which blackens when dried, and is not decomposed by acids. It is slightly soluble in water.
- 13. Sulpho-arsenite of iron gives a dark brown precipitate, almost black, which dissolves with a brown colour in an excess of the precipitating medium. When dried it becomes grayish brown, and when pulverized gives a dark brownish powder, consisting of oxide of iron united to sulpho-arsenite of bisulphuret of iron. When distilled it gives off orpiment and sulphurous acid, and leaves sulphate of iron.

¶ Ibid. ¶ Ibid. p. 290.

- 14. Sulpho-arsenite of bisulphuret of iron forms an olive green precipitate. An excess of the precipitating medium dissolves it with a black colour. When dried it is green, and it gives a fine yellowish green powder. It fuses very easily, and becomes translucent and yellowish. When heated to redness in a retort it is decomposed and leaves sulphuret of iron without any arsenic.\*
- 15. Sulpho-arsenite of manganese gives an orange precipitate which becomes dark coloured while drying. Its powder has a fine dark yellow colour. When distilled it gives out orpiment, and leaves a yellowish green substance which is not farther decomposed.
- 16. Sulpho-arsenite of nickel is a black precipitate, which retains its colour on drying and gives a black powder. When distilled it easily loses its orpiment, and leaves a yellow stalactitical sulphuret of nickel.‡
- 17. Sulpho-arsenite of cobalt gives a dark brown precipitate. The supernatant liquid has at first the same colour, but at last becomes clear. The salt is dissolved by an excess of the precipitating medium. When dried it becomes black. When distilled it gives out orpiment, and leaves a gray metallic fused mass, which contains sulphur and arsenic, and which Berzelius conjectures to be the same as glance cobalt.§
- 18. Sulpho-arsenite of zinc gives a lemon yellow bulky precipitate. When dry it is light orange. When heated to redness in a retort it gives out a portion of orpiment and leaves a yellow hard cohering substance. In the heat at which glass melts it gives out the last traces of its orpiment and leaves sulphuret of zinc.
- 19. Sulpho-arsenite of cadmium gives a light yellow precipitate, which on drying becomes a fine orange yellow. When heated it undergoes a semifusion, and when distilled gives out a portion of its orpiment, after which there remains a swollen gray metallic looking matter, becoming dark yellow when pounded, and constituting a subsalt.
- 20. Sulpho-arsenite of lead gives a red brown precipitate, which when collected becomes black. The dry salt gives a brown powder, which coheres under the pestle and becomes steel gray and splendent. It melts easily and retains its orpi-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 290.

<sup>†</sup> Ibid. p. 289. ‡ Ibid. p. 290. § Ibid.

<sup>|</sup> Ibid. p. 289. | ¶ Ibid. p. 290.

ment. The fused mass is gray and metallic, has a splendent sect. IV. crystalline fracture, and gives a gray metallic powder.\*

• 21. Sulpho-arsenite of tin gives a dark reddish brown precipitate which retains its colour when dry. It does not melt. When distilled it gives out a portion of its orpiment, leaving a gray porous metallic mass, which contains both arsenic and sulphur.+

22. Sulpho-arsenite of bisulphuret of tin forms a yellow slimy precipitate, which on drying becomes orange yellow and gives a yellow powder. When distilled it exhibits the same phenomena as the last species.‡

23. Sulpho-arsenite of copper gives a dark brown precipitate, which on drying becomes blackish brown. It coheres together when pounded, becomes gray, and assumes the metallic lustre. When distilled it gives first sulphur and then orpiment, and leaves a swollen gray half fused substance, having the metallic lustre, and giving a gray metallic powder.§

When a solution of bisulpho-arsenite of potassium is decomposed by means of hydrated oxide of copper, added as long as the liquid continues to alter its colour, we get one portion of the newly formed copper salt dissolved in water, while another remains undissolved. If the dissolved portion be thrown down by muriatic acid, we obtain a light brown precipitate, which is a compound of

1 atom sesqui-sulphide of arsenic	•	•	7.75
$l_{\frac{1}{2}}$ atom sulphuret of copper .	•	•	9
While the undiscolved nortion is compa	and of		16.75
While the undissolved portion is composite atom sesqui-sulphide of arsenic	osea oi		7.75
6 atoms sulphuret of copper .	•	•	36
o atoms surpriered to copper .	•	•	
			43.7511

24. Sulpho-arsenite of bismuth forms a reddish brown precipitate, which, when dry, becomes black. When pulverized it gives a blackish brown powder. It fuses easily, and when the temperature is augmented, gives out orpiment and leaves a fused mass, which is not farther altered. It is gray, has the metallic lustre, a crystalline fracture, and gives a gray metallic powder. It is a subsulpho-arsenite.

25. Sulpho-arsenite of mercury forms an orange red flocky precipitate, which, if the water holds an excess of corrosive sublimate, becomes speedily quite white. If there be an excess of orpiment, it retains its colour. When dried it becomes dark brown; the powder is deep yellow. It first fuses and then sublimes. The sublimate, when in thin plates, is translucent and yellowish. Its cross fracture is grayish, and has the metallic lustre. It gives a yellow powder, just as before sublimation. This sublimate is bisulpho-arsenite of mercury.\*

26. Sulpho-arsenite of disulphuret of mercury gives a black precipitate, which, when the mercurial salt contains red oxide, is grayish green. When distilled it decrepitates so rapidly as to imitate an explosion. Metallic mercury is evolved, and then the compound sublimes.†

27. Sulpho-arsenite of silver forms a light brown precipitate, at first translucent; but when it collects together it becomes black. When distilled it gives out orpiment and melts. At last the neutral salt remains, which is no farther altered. It is a black metallic mass, which, when pulverized, gives a light brown powder. If a saturated solution of chloride of silver in caustic ammonia be mixed with a bisulpho-arsenite, a dark yellow precipitate falls, which, according to Berzelius's analysis, is a compound of

102.25 ‡

- 28. Sulpho-arsenite of gold forms a yellow precipitate, which collects together, and becomes at last almost black. The powder is yellowish brown. It melts easily at a low red heat, gives out a portion of orpiment, and continues in a state of fusion. When cold it is translucent and has a dark yellowish red colour. §
- 29. Sulpho-arsenite of platinum forms a precipitate which is at first yellow; but becomes at last dark brown. When dry it is black, but gives a dark brown powder. When distilled it gives out readily a portion of its orpiment and melts. The fused mass, is black, has a glassy fracture, and gives a gray metallic powder. When heated to whiteness in a distilling apparatus, it gives out more orpiment, and coheres together to

<sup>Berzelius, Kong. Vet. Acad. Handl. 1825, p. 292.
† Ibid. † Ibid. p. 293. § Ibid. p. 294.</sup> 

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a porous mass of a lighter colour. It still retains both sulphur and arsenic, and melts easily before the blow-pipe.\*

• 30. Sulpho-arsenite of antimony forms an orange red precipitate, which fuses easily to an orange yellow translucent mass.+

- 31. Sulpho-arsenite of chromium is a smutty grayish yellow precipitate, which, when dry, is yellow, with a tint of green. It melts and gives out orpintent. The fused mass is dark gray, and gives a blackish gray powder with a shade of green. In a still higher temperature more orpiment escapes, and a pulverulent gray mass remains like sulphuret of chromium, which acquires a polish under the pestil, has a soft feel, and adheres to the skin. Heated in the open air it catches fire, and is converted into oxide of chromium, while arsenious acid and sulphurous acid make their escape.‡
- 32. Sulpho-arsenite of uranium is a dark yellow precipitate, which, when dry, has a tint of green, and when pulverized gives a smutty yellow powder. It undergoes semifusion when heated, and gives off a portion of its orpiment. When heated to whiteness in a close vessel it leaves an unfused, porous, grayish brown mass, whose powder is quite like that of reduced uranium. It is a subsulpho-arsenite of chromium.§
- 33. Sulpho-arsenite of molybdenum forms a brown precipitate, which, when they, is black, and gives a dark brown powder. When distilled it easily parts with its orpiment, and leaves sulphuret of molybdenum.

#### SECTION V. -- OF HYPOSULPHO-ARSENITES.

Realgar, which is a compound of I atom of sulphur and I atom of arsenic, has likewise the property of combining with alkaline sulphurets, and these salts may be called hyposulphoarsenites from analogy with the hyposulphites and hypophosphites, which exhibit analogous combinations among the oxygen acid salts.

This combination does not take place directly, for when realgar is digested with sulphuret of potassium, or with caustic potash, it is decomposed, and gives a dark brown powder, consisting of arsenic combined with a minimum of sulphur. When sulpho-arsenite of potassium is melted with an additional quantity of arsenic, we form hyposulpho-arsenite of potassium, which easily swells up, and the excess of arsenic makes its

<sup>•</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 293.

Class VII. escape. In water the salt is decomposed, just as when realgar is dissolved in potash.

> If orpiment be boiled with carbonate of potash or soda in a " tolerably concentrated solution, and be filtered while boiling hot, a colourless liquid passes through, which, after cooling, deposites (within 12 hours) a copious precipitate, quite similar in appearance to Kermes mixeral. This is a hyposulphoarsenite of potassium or sodium. It is soluble in water; but not so, while it contains sulpho-arsenite of potassium in solution. Let it be collected on the filter, and when the liquid has drained from it, a little pure water must be poured on it once or twice. It soon swells out, becomes gelatinous, and the liquid passes through pure yellow. The salt precipitates again, if the liquid holding it in solution be mixed with more It dries into a translucent red mass. water.

On the filter remains a dark brown powder, insoluble in water, which is a bihyposulpho-arsenite of potassium. It melts easily when heated, gives out nothing volatile, and leaves a translucent red mass, insoluble in water. Caustic potash dissolves it with the same phenomena as realgar.

When the neutral sulpho-arsenites of the bases of the alkalies and alkaline earths are exposed to spontaneous evaporation, they leave dark red insoluble compounds, which are bihyposulpho-arsenites.

With glucinum, yttrium, and aluminum, such compounds are not formed. The red solutions give light coloured precipitates with the evolution of sulphide of hydrogen.

With sulphuret of zirconium realgar unites to a dark brown precipitate, which sinks slowly. With manganese, zinc, and cerium, are obtained red or dark yellow precipitates, not like the sulpho-arseniates or sulpho-arsenites. But the remaining metals give precipitates quite similar to the sulpho-arsenites.\*

#### SECTION VI. --- OF SULPHO-MOLYBDATES.

The sulpho-molybdates consist of combinations of the alkaline sulphurets with tersulphide of molybdenum, described in vol. i. p. 360, of this work. It is analogous in its constitution to molybdic acid.

The sulpho-molybdates are most easily obtained when an oxygen salt is decomposed by sulphide of hydrogen. The decomposition goes on with difficulty in dilute solutions, but

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 295.

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rapidly in concentrated ones. The liquid becomes red like a bichromate, or (if it contain iron) reddish brown. These salts when pure have a red colour; a shade of brown indicates the presence of iron. An excess of ter-sulphide of molybdenum likewise renders the colour darker. During evaporation, the liquid emits the smell of sulphide of hydrogen; but no precipitate falls, at least at first.

When burnt, they are decomposed. Those which contain the basis of an alkali, or alkaline earth, are changed into quatersulphurets of the base, and into bisulphide of molybdenum. The salt of potassium is decomposed to the amount of twothirds, the salt of sodium farther, and the rest altogether. The sulpho-molybdates with weaker bases give out sulphur, and leave a compound of the base with bisulphide of molybdenum. When the solutions of these salts are left exposed to the air, they are but little altered when in the state of bisulpho-molybdates. But the subsalts are oxidized rapidly even in a solid form, and a molybdate with a subsulphite and sulphite is formed, leaving a neutral sulpho-molybdate. A grayish brown matter is gradually deposited, during which the beautiful colour of the solution is altered. It becomes opaque and dark brown, then greenish brown, and at last pure blue. The liquid contains a solution of sulphate and molybdate of potash, together with molybdate of molybdenum.

- 1. Sulpho-molybdate of ammonia is best obtained by decomposing molybdate of ammonia by sulphide of hydrogen. It may be formed also by dissolving molybdic acid in sulphohydrate of ammonia, or by digesting newly precipitated tersulphide of molybdenum in sulpho-hydrate of ammonia. The best way of procuring it in the solid form, is to mix a somewhat concentrated solution with alcohol, which throws it down in a cinnabar red powder. By exposure to the air, it becomes dark brown. If the aqueous solution be left to spontaneous crystallization, crystals appear round the surface of the liquid, which reflect a green light; but a great portion dries into a dark gray shining mass, not crystallized, and easily soluble in water. It consists chiefly of a bisalt. Both the neutral and bisalt are with difficulty soluble in alcohol.\*
- 2. Sulpho-molybdate of potassium. To obtain this salt, mix carbonate of potash with rather more sulphur than is requisite to make quinto-sulphuret of potassium, and with charcoal pow-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 308.

Class VII. der to decompose the sulphate of potash formed during the process. Mix the saline mass thus obtained with a great excess of native bisulphide of molybdenum. Put the mixture into a Hessian crucible, covered with charcoal powder. Heat at first so gently, that a sulphuret of potassium with excess of sulphur is formed. When no more sulphur is observed to burn round the mouth of the crucibie, the heat is augmented to redness, and continued so long as the smell of sulphurous acid is perceptible. The sulphide of molybdenum is formed from the excess of sulphur. Let the whole be raised to a white heat, and let the heat be continued for three hours. The mass, when cold, is black, porous, and unfused. When gently heated with water, it gives a deep red solution, which is quite opaque. When evaporated in a temperature of 104°, dark red crystals These are extremely beautiful, having a green colour, and the metallic lustre resembling that of the wings of the melolontha or lytta. They are four or eight-sided prisms, terminated by bihedral summits. When dissolved in water, the liquid has a fine red colour, like that of a very concentrated solution of bichromate of potash. When a hot saturated solution is left to cool, small four-sided right prisms are formed, which by reflected light are green, and have the metallic lustre, by transmitted light ruby red. The fracture of the crystal is glassy and uneven, and has the same fine green colour as the Powder fine dark red, cohering under the pestle, and becoming shining and green. It contains no water of crystallization. Alcohol precipitates this salt from its aqueous solution in the state of a cinnabar red powder, and from the liquid cinnabar red scales shoot, which when dry assume a green colour, and the metallic lustre. By the analysis of Berzelius, the constituents of this salt are

	Tersulphide of molybdenum		•	•	63.43
\$	Sulphuret of potassium .		•	•	36.57
This is	is abuianaly assimalant to				100.00
	is obviously equivalent to Latom tersulphide of molybde	num	١		12
	2	11 (414)	•	•	
I	atom sulphuret of potassium		•	•	7
					-
					19*

<sup>3.</sup> Sulpho-molybdate of sodium may be obtained by decom-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 303.

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posing neutral molybdate of soda, by means of sulphide of hydrogen. When the liquid is strongly concentrated, small granular dark red crystals are deposited, and the whole mass becomes solid. It is difficult to obtain the salt in regular crystals, but they seem to be prisms, which have a green colour. It is much more soluble in water than the potassium salt. Hence it is not precipitated when its solution is mixed with alcohol. When heated to redness, it is decomposed with a very slight residue of unaltered salt.\*

- 4. Sulpho-molybdate of Ithium is very soluble in water. When evaporated, it gives a brown syrup, which deposites no crystals on cooling. The salt remains long moist, and at last hardens to a dark red mass, which does not deliquesce in the air. When distilled, it is decomposed, and leaves, when dissolved in water, the whole molybdenum in the state of gray sulphuret. The aqueous solution contains lithium combined with 4 atoms of sulphur. It gives a bisalt like the two preceding species of sulpho-molybdates.+
- 5. Sulpho-molybdate of barium is obtained when sulphuret of barium is boiled with an excess of tersulphide of molybdenum. The solution is filtered while boiling hot, and received into a vessel previously heated. During the cooling, small fine yellow shining crystals are deposited, which on paper fall down into the state of a shining yellow meal. When gently heated, they lose water, and become red. They are not decomposed by concentrated muriatic acid while cold; but dilute muriatic acid acts upon them more easily. By the assistance of heat, sulphide of hydrogen is disengaged, and tersulphide of molybdenum. These crystals are a supersalt, composed, according to the analysis of Berzelius, of

6 atoms tersulphide of molyb	•	<b>72</b>		
1 atom sulphuret of barium				10.5
				-
				82.5

- 6. Sulpho-molybdate of strontium behaves exactly like the last species, both in its neutral state and as a supersalt.§
- 7. Sulpho-molybdate of calcium gives in the same way a supersalt, which crystallizes from the solution filtered while boiling hot. It consists of fine, short, shining, translucent, cinnabar red crystals, which are not altered by exposure to the

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 307. † Ibid. p. 308. † Ibid. p. 309. † Ibid. p. 310.

Class VII. air, nor when heated to 212°. Muriatic acid blackens them, by separating tersulphide of molybdenum. By evaporating the liquid, an additional crop of crystals are obtained. At last there remains a neutral compound, which dries to a dark red varnish.\*

- 8. Sulpho-molybdate of magnesium is obtained when tersulphide of molybdenum is boiled with sulpho-hydrate of magnesium. The solution on cooling deposites a supersalt in the form of a dark brown powder. The remaining liquid dries to a dark red varnish.+
- 9. Sulpho-molybdate of yttrium t seems to be soluble in water, as a solution of acetate of yttria is not precipitated by sulphomolybdate of potassium. In 12 hours a brown matter precipitates, which is merely tersulphide of molybdenum, and acids do not occasion an odour of sulphide of hydrogen. By this precipitate, the liquid loses its colour.§
- 10. Sulpho-molybdate of glucinum behaves in the same way, but is decomposed more slowly. Tersulphide of molybdenum falls down in twelve hours, but the liquid does not become colourless.
- 11 and 12. The salts of alumina and zirconia give immediate precipitates, which have all the appearance of tersulphide of molybdenum mixed with the precipitated earths. The liquid smells of sulphide of hydrogen.¶
- 13. Sulpho-molybdate of cerium gives a dark, almost black gray precipitate, which when dry is a dark brown powder. The liquid is colourless.\*\*
- 14. Sulpho-molybdate of sesqui-sulphuret of cerium is soluble A portion, indeed, falls of a brown colour; but most part remains in solution of a deep yellow colour.
- 15. Sulpho-molybdate of iron is soluble in water, with a fine wine red colour, which by the action of the air becomes almost A dilute solution of this salt is very easily decomposed under evaporation, and deposites a light rust yellow powder.++
- 16. Sulpho-molybdate of bisulphuret of iron falls in the form of a dark brown precipitate, which dissolves with a black colour in an excess of the precipitating medium, but generally preci-

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 310.

<sup>‡</sup> This and the following salts were obtained by Berzelius, by decomposing the neutral oxygen salts by a solution of crystallized sulpho-molybdate of potassium.

<sup>§</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 311. | Ibid.

<sup>¶</sup> Ibid. \*\* Ibid. †† Ibid. p. 312.

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pitates again in 24 hours. It is not altered while drying. When dry, it is black, and gives a brown powder; when distilled, it gives out much sulphur, and leaves a gray shining mass, resembling bisulphide of molybdenum.\*

- · 17. Sulpho-molybdate of manganese is soluble in water, and is obtained by digesting sulphuret of manganese and tersulphide of molybdenum mixed tagether in water. There must not be an excess of the sulphide. The solution is brownish yellow, and dries to a translucent varnish. The liquid is precipitated by ammonia, which separates a subsalt in the form of a red powder, which becomes brown on drying. When an excess of Ammonia is added the precipitate is decomposed to a certain extent, and it becomes black by absorbing oxygen while drying.+
- 18. Sulpho-molybdate of nickel falls with a deep brown colour, which it retains when dry. It dissolves with a black colour in the potassium, but is mostly precipitated again in 24 hours.‡
- 19. Sulpho-molybdate of cobalt behaves exactly like the nickel salt.§
- 20. Sulpho-molybdate of zinc forms a dark brown precipitate like the earthy salts. The supernatant liquid is colourless.
- 21. Sulpho-molybdate of cadmium forms a dark brown precipitate, the colour of which does not deepen on drying. liquid is colourless.¶
- 22. Sulpho-molybdate of lead is a black precipitate, black when dry, and giving a lead gray metallic streak.\*\*
  - 23. Sulpho-molybdate of tin is a black precipitate.++
- 24. Sulpho-molybdate of bisulphuret of tin is a translucent brown precipitate, which when dried becomes brownish gray. ‡‡
- 25. Sulpho-molybdate of copper forms a dark brown precipitate, almost black, which retains its colour when dry.§§
- 26. Sulpho-molybdate of bismuth is a dark brown precipitate.|| ||
- 27. Sulpho-molybdate of mercury is a light brown precipitate, which is not altered by an excess of the sulphide, but is immediately destroyed if there be an excess of corrosive sublimate. The precipitate becomes white and the liquid blue. When dry the salt gives in trituration a dark brown powder.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 312. † Ibid. p. 311. | Ibid. p. 313. ‡ Ibid. p. 312. § Ibid. ¶ Ibid.

<sup>\*\*</sup> Ibid. tt Ibid. 11 Ibid. §§ Ibid.

<sup>|| ||</sup> Ibid.

Class VII. When distilled it gives out first sulphur and then cinnabar, and leaves gray bisulphide and molybdenum.\*

28. Sulpho-nolybdate of silver is a black precipitate.

dry its streak is bluish gray and shining.+

- 29. Sulpho-molybdate of gold is soluble in water, from which in an hour it falls in the form of a dark brown powder, which blackens on drying.
- 30. Sulpho-molybdate of platinum gives a dark brown precipitate, which is almost black when dry.§
- 31. Sulpho-molybdate of chromium is a dark brown precipitate, which assumes a shade of green when dry.
- 32. Sulpho-molybdate of uranium is a dark brown precipitate, not altered by drying.

## SECTION VII. --- OF HYPERSULPHO-MOLYBDATES.

These salts are combinations of the quater-sulphide of molybdenum, described in Vol. I. p. 360 of this work, with the sulphurets.

- 1. Hypersulpho-molybdate of ammonia is obtained when quater-sulphide of molybdenum still moist is covered with sulpho-hydrate of ammonia. A yellow powder is obtained, but which becomes dark red when dried, probably from the It is soluble in loss of a portion of its sulphuretted base. boiling water, but insoluble in alkaline leys. \*\*
- 2. Hypersulpho-molybdate of potassium. This salt was obtained by Berzelius in crystals. His process was as follows: A molybdate of potash containing a great deal of bimolybdate in a somewhat dilute solution was decomposed by sulphide of hydrogen, and the solution concentrated by distillation. much precipitate fell that the liquid could no longer be boiled with ease. It was therefore allowed to cool. In the precipitate appeared small ruby red heavy crystals of hypersulphomolybdate of potassium. These crystals were very small. They were rectangular translucent plates, longitudinally striated. At the common temperature of the air they were insoluble in water, muriatic acid, and caustic potash. water dissolved them, constituting a fine red liquid, from which the hypersulpho-molybdate was precipitated by muriatic acid. When heated to incipient ignition the salt decrepitated, gave out a little water, some sulphur and sulphide of hydrogen, and

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1825, p. 313. + Ibid. p. 314.

<sup>||</sup> Ibid. p. 311. ¶ Ibid. p. 313. 1 Ibid. § Ibid.

<sup>\*\*</sup> Ibid: p. 321.

became gray and shining. Water dissolved from it only sul- Sect. VII. phuret of potassium, which was precipitated white by muriatic acid. The undissolved portion was gray bisulphide of molybdenum, which had retained the form of the crystalline plates.

When a solution of sulpho-molybdate of potassium, containing abundance of sulphur, is diluted with water and placed in a temperature of from 140° to 176° it becomes muddy and deposites a lighter coloured powder which is hyper-sulphomolybdate of potassium. When dried it is a fine yellow cohering mass, consisting of small shining crystalline grains. dissolves with great difficulty in cold water, which assumes a light yellow colour. But water heated to 176° dissolves it with a red colour, and the solution does not precipitate on cooling. When evaporated it gives a red translucent mass not in the least crystalline.\*

- 3 and 4. Hypersulpho-molybdate of sodium and lithium are formed in the same way as the preceding salt. They have quite the same external characters. They have only been obtained in the state of a yellow powder, easily soluble in boiling water.+
- 5. Hypersulpho-molybdate of barium is insoluble in water, and is precipitated when hypersulpho-molybdate of potassium is mixed with chloride of barium. The precipitate is a fine yellow with a shade of red. It is not dissolved by boiling water, but by boiling it becomes cinnabar red and falls heavy to the bottom. By dilute muriatic acid the precipitate is not altered.t
- 6. Hypersulpho-molybdate of strontium behaves like the The supernatant liquid is colourless.§
- 7. Hypersulpho-molybdate of calcium does not fall immediately when hypersulpho-molybdate of potassium is mixed with chloride of calcium; but if alcohol be added the liquid becomes slightly muddy, and in 12 hours a cinnabar red powder, insoluble in water, is deposited.
- 8. Hypersulpho-molybdate of magnesium is an insoluble red precipitate. The supernatant salt is clear and colourless.
- 9. Hypersulpho-molybdate of aluminum does not precipitate when hypersulpho-molybdate of potassium is mixed with a solution of muriate of alumina, but the liquid becomes red, and when filtered the red salt remains upon the filter and the liquid passes through colourless.\*\*
  - \* Berzelius, Kong. Vct. Acad. Handl. 1825, p. 318. † Ibid. p. 320.
  - | Ibid. ¶ Ibid. \*\* Ibid. p. 322.

- 10. Hypersulpho-molybdate of iron. The protosalts of iron are not thrown down by hypersulpho-molybdate of potassium, unless there be present an excess of iron, when a red precipitate is formed.
- 11. Hypersulpho-molybdate of tin. The deutochloride of tin is precipitated red, but a great deal of the precipitate is again dissolved in the liquid with a red colour. The protockloride of tin is precipitated, completely with a dark brown colour. But if the mixture be left for some days in an open vessel a solution takes place in consequence of the oxidizement of the tin; the hypersulpho-molybdate of tin and the liquid (formerly colourless) become red.
- 12. Hypersulpho-molybdate of copper. At first cark, but when collected it becomes red with a shade of brown.
- 13. Hypersulpho-molybdate of bismuth. A dark powder almost brown.
- 14. Hypersulpho-molybdate of mercury is similar in its appearance to the preceding salt.  $\parallel$
- 15. Hypersulpho-molybdate of silver. A dark brown powder, becoming black.¶
- 16. Hypersulpho-molybdate of gold is at first dark brown, but when dried it becomes yellow with a smutty metallic lustre, assuming a polish, a proof that the salt has undergone decomposition. By distillation the sulphur flies off and the salt becomes darker. When heated in the open air it burns with the evolution of sulphurous acid and becomes yellow. In a stronger heat molybdic acid is sublimed.\*\*

## SECTION VIII. --- OF SULPHO-TUNGSTATES.

These are salts of tersulphide of tungsten, described in Vol. I. p. 369, of this work, and corresponding in its composition to tungstic acid.

- 1. Sulpho-tungstate of ammonia is most easily formed by decomposing a concentrated solution of tungstate of ammonia, by means of sulphide of hydrogen. The sulpho-tungstate separates in light red crystals, similar in appearance to sulpho-tungstate of potassium. It decrepitates when heated, gives out water with sulphuret of ammonia, and leaves at last a gray sulphuret of tungsten, having the metallic lustre, and retaining the form of the original crystals. It is more soluble in pure water, than in water holding a salt in solution. It is partially

decomposed when left to spontaneous evaporation, and does sect. VIII. not form a double salt when dissolved together with nitrate of ammonia, and the solution left to spontaneous evaporation.\*

2. Sulpho-tungstate of potassium. It may be obtained by decomposing tungstate of potash by means of sulphide of hydrogen, and concentrating the yellow solution, by placing it in vacuo over dry potash. The salt shoots into fine yellow crys-By means of heat they dissolve in the mother ley, and when the liquid is left to spontaneous crystallization, four-sided flat prisms are deposited, terminated by two-sided summits, and having a dark red colour. This salt is anhydrous. excluded if fuses without undergoing decomposition.  $\mathbf{W}$ hile in fusion it is dark brown, but becomes yellow on cooling. When the solution is still dissolves in water without residue. mixed with alcohol, the salt is gradually deposited in small cinnabar red prisms. It is very slightly soluble in alcohol. the experiments of Berzelius, it would appear that the constituents of this salt are

1 :	atom	tersulphide of tungsten	•		18.5
1 :	atom	sulphuret of potassium	•	•	7.0
					25.5+

This salt has the property of combining with several oxygen acid salts, and of forming double salts. Of these the two following have been examined by Berzelius.

3. Sulpho-tungstate of potassium combined with nitre. attempt to decompose wolfram, and obtain tungstic acid, by means of carbonate of potash mixed with some nitre, Berzelius obtained from the solution decomposed by sulphide of hydrogen, and allowed to crystallize in vacuo, a ruby red salt of a fine colour, which redissolved, and left to spontaneous evaporation, shot into large and fine crystals of a very complex form, translucent, shining, and having a ruby red colour. These crystals constitute the salt in question. When these crystals are heated in a glass tube till they begin to melt, they detonate and leave a yellow mass, soluble in water, and consisting of a mixture of sulpho-tungstate. From the analysis of Berzelius, this salt appears to be composed of

<sup>•</sup> Berzelius, Kong. Vet. Acad. Handl. 1826, p. 61.

<sup>+</sup> Ibid. p. 56.

2 atoms sulpho-tungstate of potassium . . . 51
1 atom nitrate of potash . . . 12.75
63.75\*

4. Sulpho-tringstate of potassium combined with tangstate of potash. During the preparation of sulpho-tungstate of potassium, after concentrating the diquid, we often obtain a lemon yellow salt, in four-sided right tables. This salt contains water of crystallization. When heated it becomes darker yellow and opaque. At incipient ignition it melts without decomposition, provided the air be excluded. It dissolves easily in water with a lemon yellow colour. The solution is not precipitated by alcohol, nor does it render manganese salts muddy. An acid gives it a fire-yellow or red colour. From the analysis of

Berzelius, it appears to be a compound of

- 5. Sulpho-tungstate of sodium. It crystallizes with great difficulty, and only when very much concentrated. The crystals are irregular, have a red colour, and speedily deliquesce, by which the colour becomes lighter and passes into yellow. When there is an excess of basis the salt is soluble in alcohol. In this state it attracts moisture very rapidly from the air, and is speedily converted into an oxygen salt.‡
- 6. Sulpho-tungstate of barium is formed with difficulty, when the oxygen salt, mixed with water is decomposed by a stream of sulphide of hydrogen. The liquid becomes yellow, and after spontaneous evaporation leaves a yellow foliated crust. The solution is not precipitated by ammonia.

If newly precipitated tersulphide of tungsten be dissolved by boiling in sulphuret of barium, we obtain a yellow matter, which dries without exhibiting any marks of crystallizing. With an excess of sulphide of tungsten, we obtain a brown varnish.§

7. Sulpho-tungstate of strontium is easily formed by decomposing tungstate of strontian by means of a current of sulphide of hydrogen. The solution is yellow, and gives lemon yellow striated crystals. The liquid is not thrown down by ammonia.

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1826, p. 57. 

‡ Ibid. p. 61. 

† Ibid. p. 60. 

∮ Ibid. p. 62.

When there is an excess of tersulphide of tungsten, a brown Sect. VIII. salt is obtained, which dries to the consistency of a syrup.\*

- 8. Sulpho-tungstate of calcium may be formed by a process similar to the preceding. It does not crystallize, but dries to a dark yellow mass. It is easily soluble in water, and slightly soluble in alcohol. When there is an excess of sulphide, a reddish brown incrystallizable compound is obtained. Caustic ammonia throws down a light yellow powder which is a subsalt.
- 9. Sulpho-tungstate of magnesium is obtained in the same way as the preceding salts. The solution is easily decomposed when exposed to the air, but in a vacuum it dries to a yellow varnish, which dissolves easily in water and in alcohol. With an excess of sulphide the compound is brown, and does not crystallize. Ammonia throws down a light yellow powder, which is a subsalt.
- 10, 11, 12. The neutral salts of alumina, glucina, and yttria are neither precipitated by sulpho-tungstate of potassium, nor by the lemon yellow double salt. Hence it is probable that the sulpho-tungstates of these salts are soluble in water.
- 13. Sulpho-tungstate of cerium is deposited in 24 hours in the state of a light yellow powder. The double yellow salt occasions a similar precipitate.§
- 14. Sulpho-tungstate of zirconium forms a brownish yellow precipitate.
- 15. Sulpho-tungstate of iron is obtained by mixing sulphotungstate of potassium with sulphate of iron. The salt has a dark yellow colour, and is soluble in water.
- 16. Sulpho-tungstate of bisulphuret of iron forms a bulky dark brown precipitate, which collects into a liver brown mass, and undergoes no farther alteration. The yellow salt gives a lighter coloured solution, which in a few days undergoes decomposition, and becomes white.\*\*
- 17. Sulpho-tungstate of manganese is easily soluble in water, and the solution is yellow. †+
- 18. Sulpho-tungstate of nickel is similar to the following salt.‡‡
- 19. Sulpho-tungstate of cobalt forms a dark brown, almost opaque liquid, which in 24 hours deposites a black precipitate.§§

*	Berzelius, Kong.	Vet. Acad. Handl.	1826, p. 62.	+ Ibid.
‡	Ibid. p. 63.	§ Ibid. p. 64.	Ibid.	¶ Ibid.
**	Ibid.	†† Ibid.	‡‡ Ibid.	∮∮ Ibid.

- 20. Sulpho-tungstate of zinc is precipitated in 24 hours in the state of a dark yellow powder.\*
- 21. Sulphortungstate of cadmium falls speedily in the form of a lemon ye low powder.+
- 22. Sulpho-tungstate of lead is a dark brown precipitate, almost black. The precipitate by the yellow double salt is smutty yellow.
- 23. Sulpho-tungstate of tin is a flocky, brown, bulky precipitate.
  - 24. Sulpho-tungstate of bisulphuret of tin is precipitated in the form of grayish yellow flocks.
  - 25. Sulpho-tungstate of copper is a liver brown precipitate, which, when collected, becomes dark brown. With the yellow double salt the precipitate is darker and almost black.
  - 26. Sulpho-tungstate of bismuth is a dark brown precipitate.\*\*
  - 27. Sulpho-tungstate of mercury falls in fine yellow flocks. When there is an excess of tersulphide of tungsten the precipitate is black, and when there is an excess of the mercurial salt the precipitate is white. The neutral salt becomes darker in drying, and becomes at last yellowish brown. When pounded it becomes dark red, and assumes a polish under the pestle. When distilled it gives out sulphur, and cinnabar and sulphide of tungsten remain behind.++
  - 28. Sulpho-tungstate of disulphuret of mercury is a black precipitate.‡‡
  - 29. Sulpho-tungstate of silver is a dark brown precipitate, which becomes speedily black. When distilled it gives out sulphur, and becomes lead gray and shining. §§
  - 30. Sulpho-tungstate of gold forms a deep brown transparent liquid, which, when exposed to the open air for a couple of days, gives a shining precipitate having a black colour.
  - 31. Sulpho-tungstate of platinum gives a deep brown liquid, which remains transparent for about an hour, and then rapidly deposites a black precipitate.
  - 32. Sulpho-tungstate of chromium is, to a certain extent, soluble in water, and deposites a small quantity of a greenish brown precipitate.

* Berzelius, 1	Kong. Vet. Acad. H	andl. 1826, p. 64.	† Ibid.
‡ Ibid.	∮ Ibid.	Ibid	¶ Ibid•
** Ibid.	†† Ibid.	‡‡ Ibid.	∮∮ Ibid.
∥∥ Ibid.	¶¶ Ibid.	•	

## SECTION IX. -- OF SULPHO-TELLURATES.

•These salts consist of combinations of sulphide of tellurium with the sulphurets. Hitherto they have been examined only by Berzelius, to whom we are indebted for the first accurate examination of the sulphide of tellurium. It is best obtained by decomposing either the tellurates or the salts in which oxide of tellurium acts the part of a basis by a current of sulphide of hydrogen. A brown flocky precipitate falls, which is sulphide of tellurium. When heated in close vessels the sulphur is driven off, and pure tellurium remains behind.

- I. Sulpho-tellurate of ammonia gives, when the solution is concentrated in vacuo over potash, crystals resembling those of sulpho-tellurate of potassium, and which are decomposed by exposure to the air. Even in vacuo it is partially decomposed, because a portion of the base flies off; but the rest may be concentrated without decomposition.\*
- 2. Sulpho-tellurate of potassium, when concentrated without the contact of air, shoots into regular four-sided prisms of a dark yellow colour. A concentrated solution may be evaporated at the temperature of 104° in the open air, and it crystallizes better when thus evaporated than when cooled. The salt becomes moist in damp air, and assumes almost a black colour. It fuses easily, and is black while in a liquid state, but on cooling it becomes brownish yellow, and dissolves again in water.+
- 3 and 4. Sulpho-tellurate of sodium and lithium could not be made to crystallize. They dry in vacuo into a dark yellow mass, easily decomposed in the air, especially the lithium salt.‡
- 5. Sulpho-tellurate of barium is best obtained by boiling sulphuret of barium with sulphide of tellurium, and evaporating the solution in vacuo. The salt shoots into large, dark yellow, translucent, flat four-sided prisms. They dissolve slowly in water, and are not altered by exposure to the air. §
- 6. Sulpho-tellurate of strontium, when concentrated to the consistency of a syrup, gives marks of crystallization, and dries into a mass of a dark yellow colour, still soluble in water. It is not decomposed by exposure to the air.
- 7. Sulpho-tellurate of calcium dries to a yellow mass, not crystalline, and very easily decomposed by exposure to the air.¶

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1826, p. 70.

<sup>†</sup> Ibid.

- 8. Sulpho-tellurate of magnesium is obtained when solutions of sulpho-tellurate of barium and sulphate of magnesia are mixed and concentrated in vacuo. It gives a dark yellow crystalline mais, which is soluble, without alteration, in water, and moderately soluble in alcohol.\*
- 9. When Berzelius attempted to obtain sulpho-tellurates of the earths by mixing together, solutions of sulpho-tellurate of sodium and an oxygen acid salt of the respective earth, sulphide of hydrogen was given off, while the earths precipitated, mixed with sulphide of tellurium, in the state of a black powder. The salts of chromium and of uranium behave in exactly the same way.†
- 10. The Sulpho-tellurates of cerium, manganese, kinc, and cadmium precipitate at first with a yellow colour inclining to brown; which speedily darken, and at last assume the colour of sulphide of tellurium. When distilled they give out sulphur.‡
- 11. Sulpho-tellurate of iron is a black precipitate. Sulpho-tellurate of bisulphuret of iron, a dark brown flocky mass, which speedily concretes into a lump. It melts easily after being dried, and when ignited in a distilling vessel it gives out much sulphur, while a gray metallic mass remains. §
- 12. Sulpho-tellurate of nickel and cobalt are both precipitated of a black colour.
- 13. Sulpho-tellurates of lead, bismuth, tin, and copper are all brown or brownish yellow precipitates, which become black while drying; when distilled give out sulphur, and leave a gray metallic mass. ¶
- 14. Sulpho-tellurate of bisulphuret of tin has a much darker colour than the preceding salts.\*\*
- 15. Sulpho-tellurate of mercury and sulpho-tellurate of disulphuret of mercury are the latter yellow brown and the former dark brown.++
- 16. Sulpho-tellurate of silver is a black bulky precipitate, which, when polished, assumes the metallic lustre. When distilled it gives out sulphur, and leaves a fused, lead gray, metallic button, which is not altered when again fused in the open air. It is malleable.‡‡
- 17. Sulpho-tellurate of gold is soluble in water, with so deep a brownish yellow colour that the liquid is opaque. In about

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1826, p. 71.

<sup>†</sup> Ibid. ‡ Ibid. § Ibid. p. 72. || Ibid.

<sup>¶</sup> Ibid. \*\* Ibid. †† Ibid. †† Ibid.

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a couple of days it is mostly precipitated in black bulky flocks, which, when distilled, give out sulphur having a dark colour, and leave a fused gray alloy of tellurium and gold.\*

18. Salpho-tellurate of platinum remains long in solution with a deep brown yellow colour, but the liquid lets fall in a few days brown flocks, which become black on being dried.

# SECTION X. -- OF SULPHO-ANTIMONIATES.

There are three sulphides of antimony, namely:

Persulphide, analogous to antimonic acid, Bisulphide, analogous to antimonic acid,

· Sesqui-sulphide, analogous to oxide of antimony.

Each of these is capable of combining with sulphurets and of forming a genus of sulphur salts. These will come to be distinguished by the terms

Sulpho-antimoniates, Sulpho-antimonites, Hyposulpho-antimonites,

According to the mode of naming which we have adopted for the sulphur salts of arsenic. But the antimonial sulphur salts have not yet been investigated. Of course it is impossible to give any account of them here. The subject, however, is interesting, and is calculated to throw much light upon some of the most complicated ores in the mineral kingdom.

We are not yet acquainted with any sulpho-antimoniates; but there are two sulpho-antimonites; namely,

1. Feather ore, which used to be considered as a mere variety of common sesqui-sulphide of antimony. Its nature was first established by Mr. H. Rose, who showed it to be a sulphoantimonite of lead, composed of

2. Jamesonite, a mineral first distinguished from common sesqui-sulphide of antimony by Mohs. It is a compound of

 $1\frac{1}{2}$  atom bisulphide of antimony,

1 atom sulphuret of lead.

There are at least 5 different species of hyposulpho-antimonites, whose existence has been recognised in the mineral kingdom. These are the following:

<sup>\*</sup> Berzelius, Kong. Vet. Acad. Handl. 1826, p. 73.